A new alkylation method for heptalene-4,5-dicarboxylates and of one of their pseudoester forms

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Abstract: Dimethyl heptalene-4,5-dicarboxylates† undergo preferentially a Michael addition reaction at C(3) with -lithiated alkyl phenyl sulfones at temperatures below −50°, leading to corresponding cis-configured 3,4-dihydroheptalene-4,5-dicarboxylates (cf. Table 1, Schemes 3 and 4). The corresponding heptalenofuran-1-one-type pseudoesters of dimethyl heptalene-4,5-dicarboxylates (Scheme 5) react with [(phenylsulfonyl)methyl]lithium almost exclusively at C(1) of the furanone group (Scheme 6). In contrast to this expected behavior, the uptake of 1-[phenylsulfonyl)ethyl]lithium occurs at C(5) of the heptalenofuran-1-ones as long as they carry a Me group at C(11) (Schemes 6 and 7). The 1,4- as well as the 1,6-addition products eliminate, on treatment with MeONa/MeOH in THF, benzenesulfinate, thus leading to 3- and 4-alkylated dimethyl heptalene-4,5-dicarboxylates, respectively (Schemes 8–13). The configuration of the addition reaction of the nucleophiles to the inherently chiral heptalenes is discussed in detail (cf. Schemes 14–19) on the basis of a number of X-ray crystal-structure determinations as well as by studies of the temperature-dependence of the 1H-NMR spectra of the addition products.

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A New Alkylation Method for Heptalene-4,5-dicarboxylates and of One of Their Pseudoester Forms

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Dedicated to Conrad Hans Eugster on the occasion of his 90th birthday

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Dimethyl heptalene-4,5-dicarboxylates[3]) undergo at temperatures below –50° with α-lithiated alkyl phenyl sulfones preferentially a *Michael* addition reaction at C(3) leading to corresponding *cis*-configured 3,4-dihydroheptalene-4,5-dicarboxylates (*cf.* Table 1, *Scheme 3* and *4*). The corresponding 1-furanone type pseudoesters of dimethyl heptalene-4,5-dicarboxylates (*Scheme 5*) react with ((phenylsulfonyl)methyl)lithium almost exclusively at C(1) of the furanone group (*Scheme 6*). In contrast to this expected behaviour, occurs the uptake of (1-(phenylsulfonyl)ethyl)lithium at C(5) of the 1-furanones as long as they carry a methyl group at C(12) (*Scheme 6* and *7*). The 1,4- as well as the 1,6-addition products eliminate on treatment with MeONa/MeOH in THF benzenesulfinate, thus leading to 3- and 4-alkylated dimethyl heptalene-4,5-dicarboxylates, respectively (*Scheme 8 – 13*). The stereochemistry of the addition reaction of the nucleophiles to the inherently chiral heptalenes is discussed in detail (*cf. Scheme 14 – 19*) on the basis of a number of X-ray

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[1]) Part of the Ph.D. thesis of *Z.A.M.*, University of Zurich, 2002.

[2]) Part of the MS thesis of *P.G.*, University of Zurich, 2000.

[3]) The locants of heptalene itself are maintained throughout the whole work. See footnote 4 in [1] for reasoning.

crystal-structure determinations as well as by studies of the temperature-dependence of the ^{1}H-NMR spectra of the addition products.

1. Introduction. – Substitution reactions at the 12π-electron annulene core of heptalenes under spontaneous re-establishment of the 12π-electron skeleton, as it is well known for aromatic substitution reactions due to the recovery of aromatization energy, are unknown. The situation changes on the level of transition-metal complexes of heptalenes. In this way, *Vogel et al.* [2] synthesized, for example, heptalene-1,6-dicarbaldehyde by *Vilsmeier* formylation of the *cis*-configured bis(tricarbonyliron) complex of heptalene. This type of electrophilic substitution reaction can also be realized, however, with $Fe(CO)_3$ complexes of open-chain hexa-1,3,5-trienes (see, *e.g.*, [3]). We have recently realized an electrophilic acetoxylation reaction of a MeO substituted heptalene-4,5-dicarboxylate, taking advantage of a corresponding heptalenone as a relay compound [1]. The principle is displayed in *Scheme 1*. It demonstrates the procedure that generally has to be followed when we undertake substitution reactions at C=C bonds in aliphatic or alicyclic surroundings, where we mostly have to deal with individual addition and elimination steps or, in rarer cases, the reverse steps, respectively.

Scheme 1

Here, we report on a new alkylation procedure at C(3) or C(2) of heptalene-4,5-dicarboxylates and one of their pseudoester forms, respectively. It is based on the afore-mentioned two-step principle, using the *Michael*-addition reaction of α-lithiated alkyl phenyl sulfones in the first step and the based-catalyzed elimination reaction of benzenesulfinate in the second “re-establishment” step.

2. Results and Discussion. – 2.1. *Alkylation of Heptalene-4,5-dicarboxylates at C(3).* We knew from our earlier alkylation experiments of dimethyl heptalene-4,5-dicarboxylates with lithiomethyl phenyl and other lithiomethyl sulfones that these nucleophiles did not react exclusively with the sterically

less hindered methoxycarbonyl group at C(4), but also to a varying extent at C(3) of the heptalene skeleton in a *Michael*-type addition reaction [4][5]. We were interested therefore to find the optimal conditions for the *Michael*-addition pathway and the optimal base for the planned subsequent elimination reaction of the corresponding sulfinates (*Scheme 2*).

Scheme 2

Dimethyl heptalene-4,5-dicarboxylate (**1**) itself reacts with ((phenylsulfonyl)-methyl)lithium in THF at –78° exclusively at C(3) and so do a number of other simply substituted heptalene-4,5-dicarboxylates, leading thus in good yields to the corresponding *cis*-configured 3-((phenylsulfonyl)methyl)-3,4-dihydroheptalene-4,5-dicarboxylates as an almost 1 : 1 mixture of epimers with respect to the axis (C(5a)–C(10a)) of chirality (*Table 1*).

Table 1

However, the reaction of **9** with ((phenylsulfonyl)methyl)lithium gave as a side-product small amounts of the alkylation product of MeOOC–C(4) as the sterically less hindered ester group, a fact that we had observed already in our former experiments with heptalene-4,5-dicarboxylates with a higher number of *peri*-substituents [4]. A more detailed investigation with the heptalene-4,5-dicarboxylates **11** and **14**, derived from 1,4,8-trimethylazulene and guaiazulene, respectively, showed that the ratio of *Michael* addition at C(3) and the alkylation reaction at MeOOC–C(4) is strongly dependent on the applied reaction temperature (*Scheme 3*). The observation that the ratio *Michael* adduct to alkylation product changes substantially in favor of the latter at –20° speaks for the fact that the *Michael* addition at C(3) is reversible whereas the alkylation at MeOOC–C(4) is irreversible due to the rapid elimination of methoxide and deprotonation of the formed (phenylsulfonyl)acetyl group at C(4). The electronic nature of the (sulfonyl)methyllithium nucleophile has no great influence on the said ratio as experiments with *N,N*-diphenylmethanesulfonamide and 4-(methylsulfonyl)morpholine demonstrate.

Scheme 3

Much more effective in view of the ratio of *Michae*l addition at C(3) *versus* alkylation at MeOOC–C(4) turned out to be the presence of an α-Me substituent in ((phenylsulfonyl)methyl)lithium as experiments with (1-(phenylsulfonyl)ethyl)lithium showed (see *Scheme 4* and later). The higher nucleophilicity and steric encumbrance of the α-branched ethyllithium reactant favor distinctly its 1,4-addition in comparison with the 1,2-addition.

Scheme 4

2.2. *Alkylations of Heptalene Pseudoesters at C(5).* As we have reported already in earlier publications, heptalene-4,5-dicarboxylates can be transformed *via* their half-esters into the corresponding regioisomeric pseudoesters [6][7], which allow selective reactions at their carbonyl groups (*Scheme 5*) [5][8]. In the course of these investigations, we were quite astonished to find that the furan-1-one **25**, derived from heptalenediester **14**, reacted with ((phenylsulfonyl)methyl)lithium in the expected manner whereas its reaction with (1-(phenylsulfonyl)ethyl)lithium led to a completely unexpected product, namely, as an X-ray crystal-structure determination (see later) revealed, to the 1,6-addition product **27** (*Scheme 6*). Further experiments disclosed that a me-

Scheme 5

Scheme 6

thyl group at C(12) of the heptaleno[1,2-*c*]furan-1-ones and at the α-position of the ((phenylsulfonyl)alkyl)lithium reactants are decisive for the formation of 1,6-adducts, whereas the presence or absence of an Me group at C(6) has no significant influence on the addition of the alkyllithium nucleophile at C(5) of the heptaleno[1,2-*c*]furan-1-ones (*Scheme 7*).

Scheme 7

The crystal structure of the 1,6-adducts **30** and **31** was again determined by an X-ray diffraction analysis (see later). The reaction of furan-1-one **32** with (1-(phenylsulfonyl)ethyl)lithium gave mainly alkylation at C(1) resulting in the formation of **33**, and only small amounts of furanone **34** were identified spectroscopically.

Fig. 1

The AM1 calculated structure of furan-1-one **25** clearly reveals the reason for its propensity to undergo a 1,6-addition reaction with (1-(phenylsulfonyl)-ethyl)lithium (*Fig. 1*). The perspective view of (*P*)-**25** with the dotted *van der Waals* surface of the O-atom of the carbonyl group and Me–C(12) plainly demonstrates that the *re*-face of the carbonyl group is perfectly shielded by Me–C(12) against a nucleophilic attack. On the other hand, the *si*-face of the carbonyl group cannot take up a nucleophile since the *van der Waals* surfaces of the O-atom of the carbonyl group and Me–C(12) are touching each other, so that there is no free space for the necessary bending mode of the carbonyl group when changing from sp^2 to sp^3 hybridisation on addition of a nucleophile. Moreover, the torsion angles Θ (O=C(1)–C(12b)–C(3a)) and Θ (C(12b)–C(3a)–C(4)–C(5)) amount to 178° and 25°, respectively, ideal for the uptake of a nucleophile at C(5), which exerts no influence on the packed spatial arrangement at the carbonyl group since the $sp^2 \rightarrow sp^3$ bending mode takes place at C(5). In the case of furan-1-ones without an Me group at C(12) (*e.g.* **32**; see also [5]), the spatial interactions at the carbonyl group are strongly reduced, so that the 1,2-addition of a nucleophile at the carbonyl group is favored.

2.3. *Elimination Reactions with the 1,4- and 1,6-Adducts.* After the failure of elimination reactions of the 1,4-adduct **15** with DBU (1,3-diazabicyclo[5.4.0]undecane) or LDA (lithium di-isopropylamide) as a base in THF according to *Scheme 2*, we found that MeONa in boiling MeOH/THF was the system of choice for the wanted removal of $PhSO_2^-$, followed by base-catalyzed tautomerisation (*Scheme 8*). The formed heptalenedicarboxylate

was obtained as a thermal equilibrium mixture of **35** and its double bond shifted (DBS) isomer **35'**, which we had obtained already earlier with a number of other products by thermal reaction of 3-methylguaiazulene with dimethyl acetylenedicarboxylate in decalin at 200° (*cf.* [9]). Other leaving groups such as $Ph_2NSO_2^-$ (16% of **35**/**35'**) or $O(CH_2)_4NSO_2^-$ (0% of **35**/**35'**) were less successful. The adduct **17** could also be reacted with LDA in THF, even though the yield of **35**/**35'** (6%) was low, and **19** gave no product at all under these conditions. Further elimination reactions, which led in moderate to good yields to some new alkylated heptalenedicarboxylates are compiled in Scheme 9[4]).

Scheme 8

Scheme 9

The (phenylsulfonyl)methyl or 1-(phenylsulfonyl)ethyl moiety at C(3) of the 3,4-dihydroheptalene-4,5-dicarboxylates should principally allow the nucleophilic introduction of further alkyl groups at C(1) of the sulfonylalkyl substituents. However, the presence of MeOOC–C(4) may favor a nucleophilic alkylation at C(4). This is indeed the case. When **23** was deprotonated with NaH, followed by addition of MeI, the C(4)-methylated 3,4-dihydroheptalene-4,5-dicarboxylate **41** was obtained almost quantitatively (*Scheme 10*)[5]). Its relative configuration was determined by an X-ray crystal-structure analysis (see later). Treatment of **41** under the established elimination conditions led at least in a yield of 20% to the corresponding 3-ethylidene-3,4-dihydroheptalenedicarboxylate **42** (*Scheme 10*). Its (3*E*)-

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[4]) The standard elimination procedure applied on **21** did not lead to the formation of 3-ethylheptalenedicarboxylates **37/37'** (*Scheme 9*; R^1, R^3, R^4 = H, R^2 = Me). Due to a shortage of starting material, we could not repeat the elimination reaction of **21** with *t*-BuOK in THF (*cf.* **2** in *Scheme 9*).

[5]) We have not verified the possibility to trap the ester enolate of **23** by silylation, followed by a second deprotonation and then alkylation.

configuration follows from an *anti*-E_2 elimination of $PhSO_2^-$ of **41**[6]), which should deliver (*P**,4*R**)-**42**. However, (*M**,4*R**)-**42** is, according to AM1 calculations, at least by about 0.7 kcal·mol^{-1} energetically favored, therefore, we think that we obtained **42** in (*M**,3*E*,4*R**)-configuration as shown in *Scheme 10*.

Scheme 10

Quite astonishing was the result of the elimination reaction of **2** under our standard conditions with MeONa in MeOH/THF. Instead of the expected heptalenedicarboxylate **36**, which was found only in a small amount, we isolated its cyclic anhydride **43** in good yield (*Scheme 11*). Similarly, the heptalene sulfone **15** gave with *t*-BuOK or Et_3COK in THF nearly equal amounts of the expected diesters **35/35'** and their common cyclic anhydride **44** (*cf*. [6] for DBS in cyclic anhydrides of heptalene-1,2- and -4,5-dicarboxylic acids). We suppose that, after deprotonation at C(4), the corresponding ester enolate **A** undergoes cyclization to **B**, which then loose methoxide to yield **C**, which represents the enol ether form of the cyclic anhydride of **15**. The final step would then be the base-induced, formal elimination of $PhSO_2H$ to give the enol ether **D**. Treatment of the latter in the course of the working-up procedure with aqueous 2N HCl yields then the observed cyclic anhydride **44**. Of course, we cannot exclude that the elimination already takes place at the stage of **B** and that the oxido-product of this reaction is present in the reaction mixture before working up. In other words, the decisive step in the discussed reaction sequence is the cyclization step, which might be dependent on the intramolecular flexibility of the 3,4-dihydroheptalene-4,5-dicarboxylates. A critical

Scheme 11

Scheme 12

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[6]) The (3*E*)-configuration of **41** is thermodynamically favored by about 2.5 kcal·mol^{-1} with respect to the (3*Z*)-form of **41**.

point may also be the elimination of $PhSO_2^-$, which should be dependent on the strength of the used base. Therefore, it is conceivable that the *peri*-substituted 3-(sulfonylmethyl)-3,4-dihydroheptalene-4,5-dicarboxylates can be transformed to the corresponding heptalene-4,5-dicarboxylates with MeONa in MeOH/THF, whereas it needs the stronger bases *t*-BuOK or Et_3COK in THF to observe in addition to diester formation also the formation of the corresponding cyclic anhydride.

It turned out that heating the 5-(1-(phenylsulfonyl)ethyl)-4,5-dihydroheptaleno[1,2-*c*]furans with MeONa/MeOH in THF was also successful for the formation of the corresponding 2-ethylated heptalene-4,5-dicarboxylates by elimination of $PhSO_2H$ (*Scheme 13*).

Scheme 13

All new heptalenedicarboxylates were fully characterized spectroscopically and the structure of **45** was also determined by an X-ray diffraction analysis (see *Exper. Part*, Table 7). It is of interest to note that in the course of the elimination reaction of **31** epimerization at the axis of chirality of **31** and/or **47** took place only to an extent of 10%. On standing at ambient temperature in $CDCl_3$ solution, the 1 : 9 ratio of **47/47'** was slowly reversed. After two months, the ratio approached a value of almost 12 : 1 in favor of **47**.

2.4. *Structural Characterization of the* Michael *Addition Products*. 2.4.1. *3-Alkylated 3,4-Dihydroheptalene-4,5-dicarboxylates*. In our former reports on the reaction of higher alkylated heptalene-4,5-dicarboxylates with ((X-sulfonyl)methyl)lithium, the relative configuration of the formed 3-alkylated heptalene-4,5-dicarboxylates had been of minor concern [4][8]. We assumed that these compounds possessed relative *cis*- and *trans*-configuration with respect to the spatial arrangements of the substituents (XSO_2CH_2, COOMe) at C(3)–C(4). This view was supported by an X-ray crystal-structure determination of one of the isomers of **19** (*cf. Scheme 3*)[7]), which revealed its

[7]) See compound **6a** in *Scheme 3* of [4].

relative *cis*-configuration, whereas the relative (*M*)-configuration at the axis of chirality (C(5a)–C(10a)) had been overlooked, since it was not in the focus of our interest at that time. On this basis, and without any further investigation, we assigned the *trans*-configuration to the second isomer of **19**[8]), found in solution, and which, together with its crystallized form, was only characterized by its ^{1}H-NMR spectrum in C_6D_6[9]).

We were surprised when we found in this work that with the exception of the mixture of the two isomers of **10**, all the simply substituted 3-alkylated 3,4-dihydroheptalene-4,5-dicarboxylates, listed in *Table 1*, showed, as mixtures at ambient temperature, in their ^{1}H-NMR spectra coalescence of almost all of the signals, and it needed temperatures as low as 223 K to get sharp signals of both isomers of the *Michael* adducts. Moreover, a temperature scan in steps of 10 K between 300 to 223 K revealed that at first most of the signals of both isomers became sharp, followed finally by the signals of H–C(3) and H–C(4) of the isomers. These observations excluded the existence of *cis*/*trans* pairs of isomers, but they were in full agreement with the presence of thermally converting epimers with respect to their axis of chirality. Fortunately, we obtained crystals of one isomer each of the 1-methyl- and 1,6-dimethyl-3,4-dihydroheptalenedicarboxylate **4** and **10**, respectively, which were suitable for an X-ray crystal-structure determination (*Fig. 2* and *3*). Both compounds showed a *cis*-arrangement of the substituents at C(3) and C(4), however, with opposite relative configuration at their axis of chirality (C(5a)–C(10a)). Thus, the crystals of **4** contained the pure (*P**,3*R**,4*R**)-isomer and those of **10** the pure (*P**,3*S**,4*S**)-form[10]).

Fig. 2

Fig. 3

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[8]) See compound **6b** in *Scheme 3* of [4].

[9]) See *Table 10* in [4].

[10]) The latter, when dissolved at room temperature in C_6D_6, slowly equilibrated to a 2 : 1 mixture with its (*M**,3*S**,4*S**)-epimer.

Systematic ^{1}H- and ^{13}C-NMR analyses of all prepared dimethyl 3-(1-(X-sulfonyl)alkyl)-3,4-dihydroheptalene-4,5-dicarboxlates (*cf. Table 1, Scheme 3, 4,* and *10*) revealed that all dicarboxylates, which carried no substituent at C(6) (see **2**, **4**, **8**) appeared with relative (*P**,3*R**,4*R**)-configuration, whereas those with a Me group at C(6) (**6**, **10**, **12**, **15**, **17**, **19**, **23**, **41**) had the relative (*P**,3*S**,4*S**)-configuration. The observation that all *Michael*-addition products of the heptalene-4,5-dicarboxylates exhibit relative *cis*-configuration of the substituents at C(3)–C(4) is in agreement with the fact that the protonation of the primarily formed C(4)-ester enolates takes place in a *trans*-relationship to the bulky (1-(X-sulfonyl)alkyl) group at C(3)[11]).

Intramolecular proton transfer does not seem to play a role in the protonation step. This is evident by the fact that the alkylation experiment of the C(4)-ester enolate of **23** with MeI, which gave exclusively the C(4)-methylated product **41** with retention of configuration at C(4) (*Scheme 10*) as revealed by its X-ray crystal-structure analysis (*Fig. 4*), and which showed the same (*P**,3*S**,4*S**)-configuration at the 3,4-dihydroheptalene core as the starting material **23** (see [5] for the X-ray structure of **23**)[12]). However, the (*R**)-configured 3-(1-(phenylsulfonyl)ethyl) group of **23** underwent, obviously due to the basic conditions of the methylation reaction, complete epimerization to (*S**)-configguration in **41**.

Fig. 4

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[11]) AM1 calculations of (*P**)-**4** and (*P**)-**10**, which very well reproduced their crystal structures, showed that the $\Delta H_f°$ values of their corresponding *trans*-forms, (*P**,3*R**,4*S**)-**4** and (*P**,3*S**,4*R**)-**10**, respectively, are lying 2.1 and 2.3 Kcal·mol^{-1}, respectively, higher in energy, *i.e.*, the 3,4-*cis*-configured 3,4-dihydroheptalenes are the thermodynamically favored forms.

[12]) In this case, AM1 calculations showed the *cis*-methylation product to be 3.3 Kcal·mol^{-1} less stable than the *trans*-product, (*P**,1'*S**,3*S**,4*R**)-**41**.

The global events of the formation of the *Michael* products are very simple (*Scheme 14*). Since we found only the *cis*-3,4-dihydroheptalene-4,5-dicarboxylates, the two epimers of which represent, due to their labile axis of chirality, the thermodynamically controlled products.

Scheme 14

However, there are principally two ways by which the uptake of the nucleophile can occur. The simplest mode is shown in the scheme. It means that the axial attack of the nucleophile would take place only at one of the prochiral sites of C(3). In other words, the decisive step of the alkylation reaction happens with 100 % stereoselectivity. The other mode would be that the nucleophile attacks C(3) with a certain stereoselectivity at both of its prochiral sites (*Scheme 15*).

Scheme 15

To get more insight into these two modes, which do not alter the global stereochemical outcome, we performed a number of AM1 calculations. First of all, X-ray crystal-structure determinations as well as calculations show for heptalene-4,5-dicarboxylates an s-*cis*-conformation of the ester C=O group at C(4) in relation to the C(3)=C(4) bond with Θ of 20° and below, independent of the number of *peri*-substituents (Table 2).

Table 2

Table 3

AM1 calculations with methanide as model nucleophile show that the axial cisoid ester-enolates, formed on the *re* path, are energetically favored by 2.3 – 5.8 Kcal·mol^{-1}, compared with those resulting from the *si*-path (*Table 3*). The reason for this difference can be seen in the almost perfect s-*trans* torsion angle at C(4)–C(5) of the (*P**,*R**)-products, which allows a much better delocalization of the negative charge of the ester-enolates already in the

transition state. This torsion angle stays almost constant (around 145°) on the way to the (*P**,*S**)-ester enolates[13]). Therefore, we assume that only the *re* path and the respective *si* path are responsible for the uptake of a nucleophile at C(3) of the discussed (*P*)- and (*M*)-heptalenediesters.

The crystal structures of (*P**,3*R**,4*R**)-**4** and (*P**,3*S**,4*S**)-**10** disclose the presence of principally a third element of chirality, namely that of the helical turn of the 3,4-substituted fragment C(2)–C(3)–C(4)–C(5) with (+)-sc torsion angles of 69.5(3)° and 67.9(2)°, respectively. The fragment is part of a seven-membered ring in a boat-like conformation with C(4) in the bow position. AM1 calculations of model *Michael* adducts of diesters **1**, **3**, **5**, and **9** again with methanide as nucleophile indicate that a second conformation is possible, wherein the fragment possesses (–)-sc conformation and C(3) takes the bow position (Table 4). One recognizes that Me substituents at the heptalene core markedly influence the thermodynamic stability of the two diastereoisomers as well as the preferred conformation of their 3,4-dihydro ring. A Me group at C(6) shifts the relative configuration from (+)-sc-(*P**,3*R**,4*R**) to (+)-sc-(*P**,3*S**,4*S**), just as observed in the crystal structures of **4** and **10**. Moreover, one can see that the (+)-sc-(*P**,3*R**,4*R**) forms are without exception by 3 –

Table 4

4.8 Kcal·mol^{-1} more stable than their (–)-sc conformers. The situation is more complex for the (*P**,3*S**,4*S**)-configured diastereoisomers. In the cases with no substituent or a Me group at C(1) the (–)-sc forms are energetically slightly favored. However, a Me substituent at C(6) (or C(1) and C(6)) makes the (+)-sc conformations more stable. Taking all together, one can say that the investigated 3,4-dihydroheptalene-4,5-dicarboxylates contain two fixed ele-

[13]) See the X-ray structures of **5** and **48** with Θ(C(5a)=C(5)–C(4)–CO_2Me) of 145.3(2)° and 144.6(3)°, respectively. [Note that in these crystal structures, the atoms have been numbered as C10a=C10-C9-C12.]

ments of chirality (centers at C(3) and C(4)) and two principally dynamic elements of chirality (axes at C(5a)–C(10a) and C(3)–C(4)).

To learn more about the molecular dynamics of 3,4-dihydroheptalenes, we calculated the transition state energies of the (*P*),(*M*) and (+)-sc,(–)-sc conversion of 3,4-dihydroheptalene (*Scheme 16*) and of (*P*,3*S*,4*S*)-3,4-dihydro-1,3,6-trimethylheptalene-4,5-dicarboxylic acid (*Scheme 17*), close to the structure of the *Michael* adduct **10** with the highest number of *peri*-substituents. The AM1 calculated data for 3,4-dihydroheptalene itself show its (+)-sc-(*P*) form more stable than its diastereoisomeric (–)-sc form, and the data listed in *Table 4* indicate that substituents in positions 1, 3, 4, 5, and 6 can enlarge this energy gap up to 4.8 Kcal·mol^{-1}. The rotational barrier at the ring bond C(3)–C(4) is with 3.0 and 4.4 Kcal·mol^{-1} expectedly low and clearly below the transition state energy of 6.6 and 8.0 Kcal·mol^{-1}, respectively, for the change of configuration of the dihydroheptalene skeleton. The rotational barrier of 2.4 and 4.1 Kcal·mol^{-1} at the C(3)–C(4) bond for the above mentioned analog of **10** does not change very much in contrast to the corresponding inversion barrier of the dihydroheptalene configuration, which amounts to 16.9 and 17.5 Kcal·mol^{-1}, respectively, and are strongly dependent on the number of *peri*-substituents as known from their parent heptalenes (*cf.* [16]). The calculated data are in perfect agreement with the observed rapid, respectively, slow (*P**,3*S**,4*S**) → (*M**,3*S**,4*S**) conversion of **6** and **10** at ambient temperature in solution. Moreover, the observed mostly broad signals for H–C(3) and H–C(4) in the ^{1}H-NMR spectra of the lower substituted 3,4-dihydroheptalene-4,5-dicarboxylates speaks for an active dynamic equilibrium of the (+)-sc and (–)-sc ring conformers at the temperature range used for the NMR measurements of the 3,4-dihydroheptalene-4,5-dicarboxylates.

Scheme 16

Scheme 17

2.4.2. *5-Alkylated 3,3-Dimethoxy-4,5-dihydroheptaleno[1,2-c]furan-1(3H)-ones.* The structure and relative configuration of the 4,5-dihydroheptaleno[1,2-*c*]furane-1-ones (*P**)-**27**, (*P**)-**30**, and (*P**)-**31** were determined by X-ray crystal-diffraction analyses (see *Figs. 5* and *6* as well as Table 7). Whereas the two former structures possess the same relative configuration, has the latter (*P**,1'*S**,5*R**)-configuration. (*P**)-**27**, when dissolved in $CDCl_3$ at ambient temperature, rapidly forms a 2 : 1 mixture with its (*M**)-epimer (*Scheme 6*). The two other compounds showed no noticeable epimerization during the time of their NMR measurement in $CDCl_3$ solution at normal temperature[14]).

The different relative configuration at C(5) of the 1,6-adducts speaks for the change of the site of the uptake of the nucleophile by the heptalenofuran-1-one as shown in *Scheme 18*. Since all three compounds exhibit the same (+)-sc conformation at the C(4)–C(5) bond with Θ(C(3a)–C(4)–C(5)–C(6)) of 64.8(2)° ((*P**)-**27**)[15]), 57.6(2)° ((*P**)-**30**), and 63.0(2)° ((*P**)-**31**), it was of interest for us to look for the reason of this site selectivity. Table 5 lists the AM1 calculated $\Delta H_f°$ values of the dienolate intermediates that are formed with the model nucleophiles methanide and 2-propanide by axial attack on the *re*- and *si*-site of C(5). All relaxed intermediates show (+)-sc conformations with Θ(C(3a)=C(4)–C(5)–C(6)) in the range of 52 – 63° for the (*P**,5*S**)-forms and 42 – 49° for the (*P**,5*R**)-forms. The two intermediate dienolate structures

Scheme 18

Table 5

arising from **28** and methanide are reproduced in Fig. 7. From the axial *re* attack results the (+)-sc conformation with the added Me group in a pseudo-equatorial position, whereas the addition on the *si* site delivers the (+)-sc conformation with the Me group in pseudoaxial position. The (+)-sc-(*P**,5*S**)-

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[14]) See later for the reason.

[15]) (*P**)-**27** appears in the crystals with two different rotational orientations of the isopropyl group with respect to the heptalene core.

dienolate intermediates with methanide as nucleophile are by $\Delta\Delta H_f°$ 0.5 – 1.9 Kcal·mol^{-1} more stable than their (+)-sc-(*P**,5*R**) counterparts, a situation, which changes with the α-branched 1-methylethanide (propan-2-ide) as nucleophile where only the (+)-sc-(*P**,5*S**)-form, derived from **30**, is by 1.0 Kcal·mol^{-1} more stable than the corresponding (5*R**)-form, whereas it is the (+)-sc-(*P**,5*R**)-form in the other two cases, which is by 1.6 – 1.8 Kcal·mol^{-1} more stable. Therefore, it is reasonable to assume that indeed increasing steric interaction in the transition state of the 1,6-addition of 1-(phenylsulfonyl)ethanide to the furanones leads to a change of the site of the attack.

Fig. 7

Protonation at C(4) of the dienolate intermediates leads to the corresponding 4,5-dihydroheptaleno[1,2-*c*]furan-1-ones, which can also be regarded as furano-anellated 3,4-dihydroheptalenes. The calculated $\Delta H_f°$ of the (+)- and (–)-sc forms of the model compounds are listed in *Table 6*. One clear answer is that the (+)-sc conformers are principally more stable than the (–)-sc forms in accordance with the X-ray crystal structures of all three heptaleno[1,2-*c*]furan-1-ones. Moreover, α-alkyl branching of the substituent at C(5) is sterically slightly better accommodated by the (*P**,5*R**)-configured furan-1-ones.

We chose 3,3-dihydroxy-5,6,8,11-tetramethyl-4,5-dihydroheptaleno[1,2-*c*]furan-1(3*H*)-one as a model for **27** to get more insight into the molecular dynamics of the furano-anellated 3,4-dihydroheptalenes (*Scheme 19*). The $\Delta H_f°$ values, listed in *Table 6*, demonstrated already that the (+)-sc-(*P**,5*S**)-forms are much more stable than their (–)-sc relatives. The same is observed in the present case, where this energy difference amounts to 5.4 Kcal·mol^{-1}. The transition state for the mutual conversion of the two conformers is –115.5 Kcal·mol^{-1} above the ground states. The $\Delta H_f^{‡}$ values for the (*P*,*M*)-epimerization of the two conformers into the most stable (–)-sc-(*M**,5*S**)-form amount to 20.4 and 15.0 Kcal·mol^{-1} in excellent agreement with the obser-

vation that (*P**,5*S**)-**27** isomerizes reversibly already at room temperature in $CDCl_3$ solution to (*M**,5*S**)-**27**.

Scheme 19

3. Final Remarks. – There are at least two open points left. The first one deals with the directing and decisive steps of the base catalyzed elimination of $PhSO_2^-$ at the structurally complex dimethyl 3,4-dihydro-3-(phenylsulfonyl)-heptalene-4,5-dicarboxylate and 3,3-dimethoxy-5-(1-(phenylsulfonyl)ethyl)-4,5-dihydroheptaleno[1,2-*c*]furan-1-ones.

Deprotonation and methylation of diester **23** yields the C(4) methylated diester **41** (*Scheme 10*), which demonstrates that H–C(4) is, as expected, more acidic than H–C(3). Moreover, the base catalyzed transformation of 41 into 42 indicates that the elimination of $PhSO_2^-$ takes place as a concerted E2 process with *anti* stereochemistry. However, what happens when C(4) carries an H-atom as in all the other cases? One possibility would be that deprotonation at C(4) does not hinder the base catalyzed concerted E2 process as discussed above, taking into account that the adjacent negative charge will favor an early transition state on the reaction coordinate of the E2 process. However, the fact that we found in some cases, which we have not investigated in detail, beside the alkylated heptalenedicarboxylates also their corresponding anhydrides speaks for an “anchimeric” assistance of the elimination reaction by the neighbored methoxycarbonyl group as depicted in *Scheme 12*.

The elimination reaction of the dihydrofuran-1-ones **27**, **30**, and **31** seems to follow an concerted E2 mechanism since we have not observed an unusual reaction behavior. Nevertheless, it is remarkable that the average yield of the elimination reaction is higher in comparison with that of the dihydroheptalene-dicarboxylates, which speaks for an easier E2 process of the dihydrofuran-1-ones.

The second point touches the question whether the described alkylation process with (1-(phenylsulfonyl)alkyl)lithium as alkyl group carrier can also be

realized with normal α,β-unsaturated carbonyl system. First experiments show that (1-(phenylsulfonyl)alkyl)lithium reactants are indeed excellent *Michael* addends for α,β-unsaturated compounds such as chalcone or methyl cinnamate (*Scheme 20*) [17]. However, the formed products **50** need at least two chemical steps to re-establish unsaturation of the β-alkylated compounds **51** by elimination of benzenesulfinate.

Scheme 20

We are thankful to our NMR laboratory for specific NMR measurements and to our MS laboratory for mass spectra. Financial support of this work by the *Swiss National Science Foundation* is gratefully acknowledged.

Experimental Part

General. See [4][5][8]. All heptalene-4,5-dicarboxylates were prepared according to our published procedures, whereby the corresponding azulenes were heated at 125 – 130° with three mol-equiv. of dimethyl acetylenedicarboxylate in toluene. 1-Methylazulene gave under these conditions only 1-methylheptalene-4,5-dicarboxylate **3** (m.p. 136.0° (Et_2O)) in a yield of 25% (*cf.* [11]) and 4-methylazulene led to the formation of a 3 : 1 mixture (total yield 35%) of 6-methylheptalene-4,5-dicarboxylate **5** (m.p. 119.1 – 120.3° (Et_2O); for X-ray data, see Table 7) and its 10-methyl analog **48** (m.p. 136.9 – 137.2° (Et_2O); for X-ray data, see Table 7) (*cf.* [11]). Finally, the 1,6,10-trimethylheptalene-4,5-dicarboxylate **11** (golden yellow crystals, m.p. 139.5 – 141.0° (Et_2O)) was obtained in a yield of 35% from 1,4,8-trimethylazulene, which was prepared by established procedures from 4,8-dimethylazulene [14]. For the synthesis of the 3,3-dimethoxyheptaleno[1,2-*c*]furan-1-ones, see [6].

1. Formation of the Dimethyl 3-(1-(phenylsulfonyl)alkyl)-3,4-dihydroheptalene-4,5-dicarboxylates. – 1.1. *Standard Procedure*. Under an atmosphere of argon and under stirring, methyl or ethyl phenyl sulfone (4.00 mmol) is dissolved in THF (8 mL) and cooled to –10°. During 10 min commercial BuLi in hexane (2.5M; 1.80 mL, 4.5 mmol) is added drop by drop, whereby the temp. is raising to –2°. After 10 min, a fine colorless precipitate is formed. After a further 30 min at 0°, the solution is cooled to –78° and a solution of the heptalene-4,5-dicarboxylate (1 mmol) in THF (5 mL) is added during 5 min. The progress of the reaction is followed by chromatography (TLC; silica gel, hexane/AcOEt). After consumption of all heptalenediester, the mixture is poured on ice, acidified with aq. 2N HCl, and extracted with AcOEt. After

washing of the extract with water and then with satur. aq. NaCl solution, the extract is dried over Na_2SO_4.

1.1.1. *Dimethyl (*P**,3*R**,4**R*)- and (*M**,3*R**,4*R**)-3-((Phenylsulfonyl)methyl)-3,4-dihydroheptalene-4,5-dicarboxylate* ((*P**)- and (*M**)-**2**). A 3 : 2 mixture (0.293 g, 69%) of (*P**)- and (*M**)-**2** was obtained as yellow oil. R_f (hexane/AcOEt 2 : 1) 0.17. IR (KBr): 1733*s* (C=O, ester), 1306*s*/1148*s* (sulfone). EI-MS: 426 (15, M^+), 366 (2, [*M* – MeOCO]), 286 (10), 285 (53, $[M - (MeOCO + PhSO_2)]^+$), 272 (14), 253 (44, $[M - (MeOCO + PhSO_2 + MeOH)]^+$), 252 (85, $[M - (MeOCO + PhSO_2H + MeOH)]$), 240 (8, $[PhSO_2CH{=}CHCOOMe]^+$), 226 (12), 225 (55), 221 (16), 213 (14), 212 (10), 209 (11), 186 (54, $[C_{10}H_7COOMe]^+$), 135 (100).

*NMR data of (*P**)-***2***[16]*: ^{1}H-NMR (500MHz, $CDCl_3$): At 300 K, almost all corresponding signals of the two epimers showed coalescence; spectrum at 223 K ($CHCl_3$ at 7.260; 60 % of the (*P**)-form): 8.00 (*d*, J_o = 7.5, H_o of $PhSO_2$); 7.71 (superimp. signals of H_p of $PhSO_2$ of both forms); 7.63 (superimp. signals of H_m of $PhSO_2$ of both forms); 6.68 – 6.47 (superimp. signals of H–C(6 – 10) and of H–C(7 – 10) of (*M**)–**2**); 6.35 (*dd*, ^3J(2,1) = 11.9, ^3J(2,3) = 6.3, H–C(2)); 6.24 (*d*, ^3J(1,2) = 12.1, H–C(1)); 3.95 (*dd*, $^2J(H_S,H_R)$ = 13.7, $^3J(H_S,3)$ = 1.8, H_S–C(1')); *ca*. 3.76 (br. *s*, H–C(4); partly covered by the *s* of MeOOC–C(5) of (*M**)-**2**); 3.69 (*s*, MeOOC–C(5)); 3.50 (*s*, MeOOC–C(4)); 3.36 – 3.32 (superimp. signals of H–C(3) of both forms); 3.12 (*t*-like, $\Sigma\ ^2J(H_R,H_S) + {}^3J(H_R,3)$ = 25.7, H_R–C(1')). ^{13}C-NMR (125 MHz, $CDCl_3$, 223 K; $CDCl_3$ at 77.00): 171.45 (MeOO*C*–C(4)); 167.08 (MeOO*C*–C(5)); 52.17, 52.14 (*Me*OOC–C(4,5)).

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[16]) Atoms of the (1-(R-sulfonyl)alkyl) groups are primed.

*NMR data of (*M**)*-**2**: ^{1}H-NMR (500MHz, $CDCl_3$; 40 % of the (*M**)-form): 7.95 (*d*, J_o = 7.5, H_o of $PhSO_2$); 7.71 (superimp. signals of H_p of $PhSO_2$ of both forms); 7.63 (superimp. signals of H_m of $PhSO_2$ of both forms); 6.87 (*d*, ^{3}J(6,7) = 11.4 H–C(6)); 6.68 – 6.47 (superimp. signals of H–C(7 – 10) and of H–C(6 – 10) of (*P**)-**2**); 6.09 (*dd*, ^{3}J(2,1) = 12.1, ^{3}J(2,3) = 3.0, H–C(2)); 5.79 (*d*, ^{3}J(1,2) = 12.1, H–C(1)); 4.56 (br. *s*, H–C(4)); 3.77 (*s*, MeOOC–C(5)); 3.62 (*dd*, $^{2}J(H_S,H_R)$ = 14.6, $^{3}J(H_S,3)$ = 5.6, H_S–C(1')); 3.39 (*s*, MeOOC–C(4)); 3.56 (*dd*, $^{2}J(H_r,H_s)$ = 14.6, $^{3}J(H_r,3)$ = 7.1, H_r–C(1')); 3.36 – 3.32 (superimp. signals of H–C(3) of both forms). ^{13}C-NMR (125 MHz, $CDCl_3$, 223 K; *C*DCl_3 at 77.00): 172.08 (MeOO*C*–C(4)); 166.16 (MeOO*C*–C(5)); 52.42, 52.27 (*Me*OOC–C(4,5)).

1.1.2. *Dimethyl (*P**,1'*R**,3*S**,4**S*)- and (*M**,1'*R**,3*S**,4*S**)-3-((1-Phenylsulfonyl)ethyl)-3,4-dihydroheptalene-4,5-dicarboxylate* ((*P**)- and (*M**)-**21**). Heptalene-diester **1** (1.00 g, 3.70 mmol) was reacted with ethyl phenyl sulfone (0.95g, 5.56 mmol) in the usual manner. The product was extracted with Et_2O and further purified by SC (SiO_2, hexane/AcOEt 2 :1), which gave 1.10 g (67 %) of a dark brown oil. The NMR analysis showed that the oil consisted of (*P**)- and (*M**)-**21** in a ratio of *ca*. 45 : 55. No signals were identified that could be assigned to **22** (see *Scheme 5*).

*Data of (*P**)- and (*M**)*-**21**: IR (KBr): 1733*s* and 1700*s* (C=O, ester), 1305*s* and 1146*s* (sulfone). ^{1}H-NMR (300 MHz, $CDC1_3$, 300 K; identified signals): 7.9 – 7.5 (H of $PhSO_2$ of both forms); 6.85 (*d*, ^{3}J(6,7) = 11.3, H–C(6) of (*M**)-form); 6.65 – 6.30 (superimp. signals of both forms); 6.05 (*dd*, ^{3}J(2,1) = 12.2, ^{3}J(2,3) = 2.7, H–C(2) of (*P**)-form); 4.47 (br. *s*, H–C(4) of (*M**)-form); 4.06 (*q*, ^{3}J(1',Me–C(1') = 7.1, H–C(1') of (*M**)-form); 3.70 and 3.37 (2*s*, MeOOC–C(4,5) of (*M**)-form);); 3.65 and 3.43 (2*s*, MeOOC–C(4,5) of (*P**)-form); 1.22 (*d*, ^{3}J(Me–C(1'),1') = 7.1, Me–C(1') of

both forms). ^{13}C-NMR (75 MHz, $CDC1_3$; identified signals)[16]): 171.69 (MeOO*C*–C(4) of (*M**)-form); 171.00 (MeOO*C*–C(4) of (*P**)-form); 167.11 (MeOO*C*–C(5) of (*P**)-form); 166.35 (MeOOC–C(5) of (*M**)-form); 147.16 (C(5a) of (*M**)-form); 145.73 (C(5a) of (*P**)-form); 63.87 (C(1') of (*M**)-form); 60.11 (C(1') of (*P**)-form); 13.99 (Me–C(1') of (*P**)-form); 13.08 (Me–C(1') of (*M**)-form). CI-MS: 458.1 (37, $[M + NH_4]^+$), 441.1 (100, $[M + l]^+$), 409.1 (43, $[(M + 1) - CH_3OH]^+$), 299.1 (67, $[(M + 1) - PhSO_2H)]^+$), 272.1 (15, $[(M + l) - C_6H_5SO_2CHMe]^+$), 187.0 (28 $[C_{10}H_8COOMe]^+$).

1.1.3. *Dimethyl (*P**,3*R**,4**R*)- and (*M**,3*R**,4*R**)-1-Methyl-3-((phenylsulfonyl)-methyl)-3,4-dihydroheptalene-4,5-dicarboxylate* ((*P**)- and (*M**)-**4**). Heptalenediester **3** (0.200 g, 0.70 mmol) gave after reaction and crystallization (hexane/AcOEt) 0.206 g (67%) colorless crystals of (*P**)-**4** (m.p. 157°) as shown by an X-ray crystal-structure determination (*Fig. 2* and *Table 7*). In $CDCl_3$ solution at ambient temp., a *ca*. 45 : 55 mixture of (*P**)- and (*M**)-**4** was formed within minutes and the corresponding signals of the epimers showed coalescence. R_f (hexane/AcOEt 2 : 1) 0.16.

Data of (*P**)-**4**: IR (KBr): 1712*s* (C=O, ester), 1334*s* and 1155*s* (sulfone). ^{1}H-NMR (700 MHz, $CDCl_3$, 270 K; 45% of the (*P**)-form; C*H*Cl_3 at 7.276): 8.02 (*d*, J_o = 7.6, H_o of $PhSO_2$); 7.702 (*t*, H_p of $PhSO_2$); 7.63 (*t*, J_o = 7.6, H_m of $PhSO_2$); 6.53 (*dd*, $^3J(9,10) \approx 7$, $^3J(9,8) \approx 11$, H–C(9)); 6.52 (*d*, $^3J(10,9) \approx 6$, H–C(10)); 6.46 (*dd*, $^3J(7,8)$ = 6.3, $^3J(7,6)$ = 11.1, H–C(8)); 6.29 (*d*, $^3J(2,3)$ = 5.3, H–C(2)); 3.96 (*d*, $^2J(H_S,H_R)$ = 13.4, H_S–C(1')); 3.80 (br. *s*, partly covered by the *s* of MeOOC–C(5) of (*M**)-**4**, H–C(4)); 3.50 (*s*, MeOOC–C(5)); 3.43 (br. *s* with spike amid, H–C(3)); 3.37 (*s*, MeOOC–C(4)); 3.07 (*t*-like, $\Sigma\ ^2J(H_R,H_S) + {}^3J(H_R,3)$ = 26.5, H_R–C(1')); 1.94 (*s*, Me–C(1)). ^{13}C-NMR (176 MHz, $CDCl_3$, 270 K; *C*DCl_3 at 77.02): 171.45 (MeOO*C*–C(4)); 166.57 (MeOO*C*–C(5)); 148.71 (C(5a)); 139.27 (C_{ip} of $PhSO_2$); 133.71 (C_p of $PhSO_2$);

132.50 (C(1)); 131.29 (C(10a)); 131.06 (C(6)); 130.15 (C(2)); 129.34 (C_m of $PhSO_2$); 129.10 (C(7)); 128.48 (C(7)); 128.03 (C_o of $PhSO_2$)); 125.81 (C(8)); 125.61 (C(9)); 120.20 (C(5)); 57.99 (C(1')); 51.93 (*Me*OOC–C(5)); 51.88 (*Me*OOC–C(4)); 44.56 (C(4)); 34.10 (C(3)); 27.37 (*Me*–C(1)). EI-MS: 440 (6, M^+), 299 (32, [M – (MeOCO + $PhSO_2$)]$^+$), 267 (6), 239 (10), 201 (11), 200 (100, [$MeC_{10}H_6COOMe$]$^+$). Anal. calc. for $C_{24}H_{24}O_6S$ (440.48): C 65.44 , H 5.49, S 7.28; found: C 65.36, H 5.43, S 7.41.

*Data of (*M*)*-**4**: ^{1}H-NMR (700 MHz, $CDCl_3$, 270 K; 55% of the (*M*)-form): 7.97 (*d*, J_o = 7.6, H_o of $PhSO_2$); 7.698 (*t*, H_p of $PhSO_2$); 7.61 (*t*, J_o = 7.7, H_m of $PhSO_2$); 6.76 (*d*, ^3J(6,7) = 11.1, H–C(6)); 6.69 (*dd*, ^3J(9,10) = 7.1, ^3J(9,8) = 10.5, H–C(8)); 6.66 (*d*, ^3J(10,9) = 6.8, H–C(10)); 6.63 (*dd*, ^3J(8,9) = 10.6, ^3J(8,7) = 6.5, H–C(8)); 6.43 (*dd*, ^3J(7,8) = 6.5, ^3J(7,6) = 10.8, H–C(7)); 5.64 (*s*, H–C(2)); 4.34 (br. *s*, H–C(4)); 3.79 (*s*, MeOOC–C(5)); 3.65 (*dd*, $^2J(H_S,H_R)$ = 14.6, $^3J(H_S,3)$ = 5.5, H_S–C(1')); 3.55 (*dd*, $^2J(H_R,H_S)$ = 14.6, $^3J(H_R,3)$ = 6.8, H_R –C(1')); 3.37 (*s*, MeOOC–C(4)); 3.29 (br. *s*, H–C(3)); 1.86 (*s*, Me–C(1)). ^{13}C-NMR (176 MHz, $CDCl_3$, 270 K; *C*DCl_3 at 77.02): 171.98 (MeOO*C*–C(4)); 165.83 (MeOO*C*–C(5)); 149.03 (C(5a)); 139.13 (C_{ip} of $PhSO_2$); 133.83 (C_p of $PhSO_2$); 132.55 (C(1)); 132.32 (C(10a)); 130.56 (C(8)); 130.17 (C(9)); 129.34 (C_m of $PhSO_2$); 129.14 (C(2) and C(10)); 128.00 (C_o of $PhSO_2$)); 125.86 (C((6)); 125.36 (C(7)); 122.67 (C(5)); 60.44 (C(1')); 52.17 (*Me*OOC–C(5)); 52.02 (*Me*OOC–C(4)); 45.80 (C(4)); 34.19 (C(3)); 26.83 (*Me*–C(1)).

1.1.4. *Dimethyl (*P**,3*S**,4*S**)- and (*M**,3*S**,4*S**)-6-Methyl-3-((phenylsulfonyl)-methyl)-3,4-dihydroheptalene-4,5-dicarboxylate* ((*P**)- and (*M**)-**6**). The standard procedure gave after crystallization (hexane/AcOEt) colorless crystals of (*P**)-**6** (0.295 g, 67%; m.p. 157°). In $CDCl_3$ solution at ambient temp., a 3 : 1 ratio of (*P**)-

and (*M**)-**6** was established within minutes. Over a longer period, the ratio approached a final value of 3 : 2. R_f (hexane/AcOEt 2 : 1) 0.14.

*Data of (*P**)*-**6**: IR (KBr): 1743*s* (C=O, ester), 1309*s* and 1132*s* (sulfone). ^{1}H-NMR (500 MHz, $CDCl_3$, 250 K; 75 % of the (*P**)-form): 8.01 (*dd*-like, $J_o \approx 7.3$, $J_m \approx 1.4$, H_o of $PhSO_2$); 7.71 (*tt*-like, H_p of $PhSO_2$); 7.63 (*t*-like, H_m of $PhSO_2$); 6.53 – 6.48 (5 line *m*, of H–C(8,9) and H–C(8) of (*M**)-form); 6.40 (*d*, ^3J(10,9) = 6.9, H–C(10)); 6.33 (*dd*, ^3J(2,1) = 11.7, ^3J(2,3) = 6.4, H–C(2)); 6.29 – 6.27 (br., slightly structured signal, H–C(7) of both forms); 6.23 (*d*, ^3J(1,2) = 11.7, H–C(1)); 4.03 (*dd*, $^2J(H_S,H_R)$ = 14.1, $^3J(H_S,3)$ = 1.9, H_S–C(1')); 3.91 (*d*, ^3J(4,3) = 2.1, H–C(4)); 3.71 (*s*, MeOOC–C(5)); 3.47 (*s*, MeOOC–C(4)); 3.36 – 3.32 (br., slightly structured signal, H–C(3)); 3.08 (*dd*, $^2J(H_R,H_S)$ = 14.0, $^3J(H_R,3)$ = 11.7, H_R –C(1')); 2.03 (*d*, ^4J(Me–C(6),7) ≈ 0.8, Me–C(6)). ^{13}C-NMR (125 MHz, $CDCl_3$, 250 K, 75 % of (*P**)-**6**; *C*DCl_3 at 77.00;): 171.00 MeOO*C*–C(4)); 168.16 (MeOO*C*–C(5)); 149.32 (C(5a)); 138.62 (C_{ip} of $PhSO_2$); 133.83 (C_p of $PhSO_2$); 133.55 (C(2)); 131.14 (C(6)); 129.95 (C(8)); 129.88 (C(10)); 129.23 (C_m of $PhSO_2$); 128.70 (C(10a)); 128.11 (C(1)); 128.07 (C_o of $PhSO_2$); 127.69 (C(9)); 124.26 (C(7)); 122.48 (C(5)); 58.57 (C(1')); 52.40 (*Me*OOC–C(5)); 52.06 (*Me*OOC–C(4)); 46.09 (C(4)); 31.80 (C(3)); 24.88 (*Me*–C(6)). EI-MS: 440 (51, M^+), 300 (8), 299 (44, [*M* – (MeOCO + $PhSO_2$)]$^+$), 283 (8), 240 (6, [$PhSO_2CH$=CHCOOMe]$^+$), 239 (26), 209 (10), 208 (10), 207 (31), 201 (13), 200 (100, [$MeC_{10}H_6COOMe$]$^+$). Anal. calc. for $C_{24}H_{24}O_6S$ (440.48): C 65.44, H 5.49, S 7.28; found: 65.38, H 5.42, S 7.35.

*Data of (*M**)*-**6**: ^{1}H-NMR (500MHz, $CDCl_3$, 250 K; 25% of the (*M**)-form): 7.98 (*dd*-like, $J_o \approx 7.3$, $J_m \approx 1.4$, H_o of $PhSO_2$); 7.69 (*tt*-like, H_p of $PhSO_2$); 7.61 (*t*-like, H_m of $PhSO_2$); 6.50 (signals of H–C(8), mostly covered by those of H–C(8,9) of (*P**)-**6**);

6.39 (*dd*, ^3J(9,8) = 11.3, ^3J(9,10) = 6.9, H–C(9)); 6.31 (*d*, H–C(10), partly covered by the signals of H–C(2) of (*P**)-**6**); 6.29 – 6.27 (br., slightly structured signal, H–C(7) of both forms); 6.10 (*dd*, ^3J(2,1) = 11.9, ^3J(2,3) = 3.1, H–C(2)); 5.83 (*dt*-like, ^3J(1,2) = 11.9, H–C(1)); 4.35 (*d*-like, ^3J(4,3) ≈ 1.2, H–C(4)); 3.80 (*s*, MeOOC–C(5)); 3.475 (br. signal, mostly covered by the signal of MeOOC–C(4) of (*P**)-**6**, H–C(3)); 3.58 and 3.57 (ABX, $^2J_{AB}$ = 14.4, $^3J_{AX}$ = 4.3, $^3J_{BX}$ = 8.5, H_S- and H_R–C(1')); 3.40 (*s*, MeOOC–C(4)); 2.09 (br. *s*, Me–C(6)). ^{13}C-NMR (125 MHz, $CDCl_3$, 250 K, 25 % of (*M**)-**6**; *C*DCl_3 at 77.00;): 171.87 MeOO*C*–C(4)); 166.42 (MeOO*C*–C(5)); 151.21 (C(5a)); 139.06 (C_{ip} of $PhSO_2$); 133.96 (C_p of $PhSO_2$); 133.52 (C(1)); 132.13 (C(6)); 130.54 (C(8)); 129.38 (C_m of $PhSO_2$); 129.54 (C(10)); 128.59 (C(10a)); 127.89 (C_o of $PhSO_2$); 126.47 (C(9)); 125.87 (C(2)); 123.82 (C(5)); 123.00 (C(7)); 58.57 (C(1')); 52.40 (*Me*OOC–C(5)); 52.06 (*Me*OOC–C(4)); 46.09 (C(4)); 31.80 (C(3)); 24.88 (*Me*–C(6)).

1.1.5. *Dimethyl (*P*,*3*R*,*4**R*)- and (*M*,*3*R*,*4*R**)-8-Methyl-3-((phenylsulfonyl)-methyl)-3,4-dihydroheptalene-4,5-dicarboxylate* ((*P**)- and (*M**)-**8**). Heptalenediester **7** (0.200 g, 0.70 mmol) was reacted with methyl phenyl sulfone (0.440 g, 2.81 mmol) according to the standard procedure to give a *ca*. 3 : 2 mixture of (*P**)- and (*M**)-**8** as a yellow oil. R_f (AcOEt/hexane 1 : 2) 0.18. IR (KBr): 1730*s* (C=O, ester), 1308*s*/1150*s* (sulfone).

*NMR data of (*P**)*-**8**: ^{1}H-NMR (500 MHz, $CDCl_3$): At 300 K, coalescence of the corresponding signals of (*P**)- and (*M**)-**8** was observed; spectrum at 223 K (C*H*Cl_3 at 7.260; 60% of the (*P**)-form): 7.98 (d, J_o = 7.5, H_o of $PhSO_2$); 7.69 (superimp. signals of H_p of $PhSO_2$ of both forms); 7.60 (superimp. signals of H_m of $PhSO_2$ of both forms); 6.52 (*d*, ^3J(6,7) = 11.7, H–C(6)); 6.49 (*d*, ^3J(9,10) = 7.7, H–C(9)); 6.40 (*d*,

^3J(10,9) = 7.6, H–C(10)); 6.29 (*d*, ^3J(7,6) = 11.4, H–C(7)); 6.25 (*dd*, ^3J(2,1) = 12.0, H–C(2)); 6.19 (*d*, ^3J(1,2) = 12.1, H–C(1)); 3.93 (*dd*, $^2J(H_S,H_R)$ = 13.7, $^3J(H_S,3)$ = 1.9, H_S–C(1')); 3.75 (br. *s*, H–C(4)); 3.67 (*s*, MeOOC–C(5)); 3.49 (*s*, MeOOC–C(4)); 3.34 – 3.28 (superimp. signals of H–C(3) of both epimers); 3.11 (*t*-like, Σ $^2J(H_R,H_S)$ + $^3J(H_R,3)$ = 25.9, H_R–C(1')); 2.08 (Me–C(8)). ^{13}C-NMR (125 MHz, $CDCl_3$, 223 K; *C*DCl_3 at 77.00; assigned signals): 171.52 (MeOO*C*–C(4)); 167.06 (MeOOC–C(5)); 147.91 (C(5a)); 141.55 (C(8)); 138.16 (C_{ip} of $PhSO_2$); 119.15 (C(5)); 58.39 (C(1')); 52.09 (*Me*OOC–C(5)); 52.02 (*Me*OOC–C(4)); 46.32 (C(4)); 31.71 (C(3)); 24.75 (*Me*–C(8)).

*NMR data of (*M**)-***8**: ^{1}H-NMR (500 MHz, $CDCl_3$, 223 K; 40% of the (*M**)-form): 7.93 (*d*, J_o = 7.5, H_o of $PhSO_2$); 7.69 (superimp. signals of H_p of $PhSO_2$ of both forms); 7.60 (superimp. signals of H_m of $PhSO_2$ of both forms); 6.83 (*d*, ^3J(6,7) = 11.9, H–C(6)); 6.40 (*d*, ^3J(9,10) = 7.7, H–C(6)); 6.34 (*d*, ^3J(10,9) ≈ 7.6, H–C(10)); 6.25 (*d*, ^3J(7,6) = 11.4, H–C(6)); 6.09 (*dd*, ^3J(2,1) = 12.2, ^3J(2,3) = 2.8, H–C(2)); 5.70 (d, ^3J(1,2) = 12.1, H–C(1)); 4.56 (br. *s*, H–C(4)); 3.75 (*s*, MeOOC–C(5)); 3.62 (*dd*, $^2J(H_S,H_R)$ = 14.7, $^3J(H_S,3)$ = 5.7, H_S–C(1')); 3.53 (*dd*, $^2J(H_R,H_S)$ = 14.7, $^3J(H_R,3)$ = 7.2, H_R–C(1'); 3.40 (*s*, MeOOC–C(4)); 3.34 – 3.28 (superimp. signals of H–C(3) of both epimers); 2.07 (Me–C((8)). ^{13}C-NMR (125 MHz, $CDCl_3$, 223 K; assigned signals): 172.06 (MeOO*C*–C(4)); 166.22 (MeOO*C*–C(5)); 147.65 (C(5a)); 141.80 (C(8)); 138.20 (C_{ip} of $PhSO_2$); 121.70 (C(5)); 60.50 (C(1')); 52.27 (*Me*OOC–C(5)); 52.20 (*Me*OOC–C(4)); 47.54 (C(4)); 32.38 (C(3)); 24.69 (*Me*–C(8)).

1.1.6. *Dimethyl* (*P**,3*S**,4*S**)- *and (*M**,3*S**,4*S**)-1,6-Dimethyl-3-((phenylsulfonyl)-methyl)-3,4-dihydroheptalene-4,5-dicarboxylate* ((*P**)- and (*M**)-**10**). The reaction of heptalenediester **9** with methyl phenyl sulfone under standard conditions delivered

after chromatography orange colored crystals of methyl 1,6-dimethyl-4-((phenylsulfamoyl)acetyl)heptalene-5-carboxylate (0.011 g, 2.6%) and colorless crystals of (*P**)-**10** (0.280 g, 62%).

*Data of (*P**)*-**10**: M.p. 163 – 164° (AcOEt/hexane). R_f (AcOEt/hexane 1 : 2) 0.13. On standing at r.t. in C_6D_6 solution, (*P**)-**10** formed a 2 : 1 mixture of (*P**)- and (*M**)-**10**. ^{1}H-NMR (600 MHz, C_6D_6, 300 K, 67% of (*P**)-**10**; C_6D_5H at 7.160): 8.04 (*d* with f.s., $J_o \approx 7.3$, H_o of $PhSO_2$); 6.97 – 6.93 (superimp. signals of H_m of $PhSO_2$ with those of H_m and H_p of (*M**)-**10**); 6.91 (*t* with f.s., $J_o \approx 7.6$, H_p of $PhSO_2$); 6.61 (*d* with f.s., $^3J(7,8) = 5.9$, H–C(7)); 6.25 – 6.23 (superimp. signals of H–C(8,9) with one of (*M**)-**10**); 6.15 – 6.12 (superimp. signal of H–C(10) with two of (*M**)-**10**); 5.99 (*dd*-like, $^3J(2,3) = 3.4$, ^4J(2,Me–C(1)) = 1.4, H–C(2)); 4.78 (*dd*, $^2J(H_S,H_R) = 14.0$, $^3J(H_S,3) = 1.9$, H_S–C(1')); 3.72 (*d*, $^3J(4,3) = 2.4$, H–C(4)); 3.68 – 3.61 (superimp. signals of H–C(3) of both epimers); 3.36 (*dd*, $^2J(H_R,H_S) = 14.0$, $^3J(H_R,3) = 11.4$, H_R–C(1')); 3.22 (*s*, MeOOC–C(5)); 3.09 (*s*, MeOOC-C(4)); 1.76 (*d*-like, ^4J(Me–C(1),2) ≈ 1, Me–C(1)); 1.71 (*s*, Me–C(6)). EI-MS: 454 (22, M^+), 315 (5), 281 (7), 253 (5), 249 (4), 221 (8), 215 (14), 214 (100, $[Me_2C_{10}H_5COOMe]^+$). Anal. calc. for $C_{25}H_{26}O_6S$ (454.51): C 66.06, H 5.76, S 7.05; found: C 65.90, H 5.73, S 7.19.

The structure of (*P**)-**10** was finally established by an X-ray crystal-structure determination (see *Table 7* and *Fig. 3*).

*Data of (*M**)*-**10**: ^{1}H-NMR (600 MHz, C_6D_6, 300 K, 33% of (*M**)-**10**): 7.83 (*d* with f.s., $J_o \approx 8$, H_o of $PhSO_2$); 6.97 – 6.93 (superimp. signals of H_m and H_p of $PhSO_2$ with those of H_m of (*M**)-**10**); 6.91 (*t* with f.s., $J_o \approx 7.6$, H_p of $PhSO_2$); 6.61 (*d* with f.s., $^3J(7,8) = 5.9$, H–C(7)); 6.25 – 6.23 (superimp. signals of H–C(10) with those of two H of (*P**)-**10**); 6.15 – 6.12 (superimp. signals of H–C(8,9) with one H of (*P**)-**10**); 6.04

(*d*, ^3J(7,8) = 6.2, H–C(7)); 5.64 (*s* with f.s., H–C(2)); 4.63 (*d* with f.s., ^3J(4,3) = 3.1, H–C(4)); 3.75 (*dd*, ^{2}J(H_S,H_R) = 14.3, ^3J(H_S,3) = 6.2, H_S–C(1')); 3.68 – 3.61 (superimp. signals of H–C(3) of both epimers); 3.51 (*dd*, ^2J(H_R,H_S) = 14.3, ^3J(H_R,3) = 6.5, H_R–C(1')); 3.35 (*s*, MeOOC–C(5)); 3.13 (*s*, MeOOC-C(4)); 2.00 (*s*, Me–C(6)); 1.67 (*dd*, ^4J(Me–C(1),2) = 1.4, ^5J(Me–C(1),10) = 2.2, Me–C(1)).

Data of methyl 1,6-dimethyl-4-((phenylsulfamoyl)acetyl)heptalene-5-carboxylate: M.p. 216.7 – 217.1° (CH_2Cl_2/hexane). R_f (AcOEt/hexane 1 : 2) 0.07. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.89 – 7.86 (H_o of $PhSO_2$); 7.66 – 7.50 (H_p and H_m of $PhSO_2$); 7.33 (*d*, ^3J(3,2) = 5.6, H–C(3)); 6.48 (signals of H–C(8,9); 6.24 (*dd*-like, ^3J(2,3) = 6.3, ^4J(2,Me–C(1)) = 1.4, H–C(2)); 6.19 (signals of H–C(7)); 5.94 (signals of H–C(10)); 4.48 and 4.44 (AB, J_{AB} = 14.1, $PhSO_2CH_2$); 3.59 (*s*, MeOOC–C(5)); 2.09 and 2.05 (2*s*, Me–C(1,6)). EI-MS: 422 (22, M^+), 313 (9), 281 (51, [M – $PhSO_2$]$^+$), 249 (39, [M – ($PhSO_2$ + MeOH)]$^+$), 239 (11), 221 (19, [M – ($PhSO_2$ + MeOH + CO)]$^+$), 214 (34), 179 (48), 156 (100, [$Me_2C_{10}H_6$]$^+$), 152 (20), 77 (20, Ph).

1.1.7. *Dimethyl (*P**,3*S**,4*S**)- and (*M**,3*S**,4*S**)-9-Isopropyl-1,6-dimethyl-3-((phenylsulfonyl)methyl)-3,4-dihydroheptalene-4,5-dicarboxylate ((*P**)- and (*M**)-***16****) and Methyl 9-Isopropyl-1,6-dimethyl-4-((phenylsulfamoyl)acetyl)heptalene-5-carboxylate* (**16**) [5]. We repeated the formerly described reaction with methyl phenyl sulfone (1.02 g, 6.50 mmol) and heptalenediester **14** (1.00 g, 2.94 mmol) according to the above given standard procedure. Workup and chromatography (silica gel, hexane/AcOEt 3 : 1) gave after crystallization from AcOEt/hexane 2 : 1 colorless crystals of (*P**)-**15** (0.470 g, 35%) and orange colored crystals of **16** (0.306 g, 24%). At ambient temperature, in $CDCl_3$ solution, (*P**)-**15** epimerized rapidly to a 3 : 1 mixture with (*M**)-**15**.

*Data of (*P**)*-**15**: See [5]. ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K, in the presence of 25% of its epimer; C*H*Cl_3 at 7.260): 8.02 – 7.97 (H_o of $PhSO_2$ of both epimers); 7.69 – 7.65 (H_p of $PhSO_2$ of both epimers); 7.64 – 7.55 (H_m of $PhSO_2$ of both epimers); 6.38 (*s*, H–C(10)); 6.28 (*d*, ^{3}J(8,7) = 6.6, H–C(8)); 6.20 (*dd*, ^{3}J(2,3) = 5.8, ^{4}J(2,Me–C(1)) = 1.0, H–C(2)); 6.15 (*dd*, ^{3}J(7,8) = 6.5, ^{4}J(7,Me–C(6)) = 1.2, H–C(7)); 4.01 (*dd*, $^{2}J(H_S,H_R)$ = 14.1, $^{3}J(H_S,3)$ = 1.9, H_S–C(1')); 3.88 (*d*, ^{3}J(4,3) = 2.5, H–C(4)); 3.68 (*s*, MeOOC–C(5)); 3.46 (*s*, MeOOC–C(4)); *ca*. 3.43 (br. *s*, mostly covered by ester signals of both epimers, H–C(3)); 3.04 (*dd*, $^{2}J(H_R,H_S)$ = 14.1, $^{3}J(H_R,3)$ = 11.4, H_R–C(1')); 2.55 (*sept*, Me_2C*H*–C(9)); 1.98 (*s*, Me–C(6)); 1.90 (s, Me–C(1)); 1.13/1.11 (2*d*, superimp. to *t*, J_{vic} = 6.8, *Me*$_2$CH–C(9)). ^{13}C-NMR (75 MHz, $CDCl_3$, 300 K; assigned signals): 170.98 (MeOO*C*–C(4)); 167.43 (MeOO*C*–C(5)); 151.52 (C(5a)); 146.88 (C(9)); 139.83 (C_{ip} of $PhSO_2$); 58.41 (C(1')); 51.84 (*Me*OOC–C(5)); 51.64 (*Me*OOC–C(4)); 44.77 (C(4)); 35.83 (Me_2*C*H–C(9)); 34.13 (C(3)); 26.10 (*Me*-C(1)); 23.45/22.41 (*Me*$_2$CH–C(9)); 23.28 (*Me*–C(6)). The full analysis of the ^{1}H-NMR shows that the crystals contain the (*P**,3*S**,4*S**)-epimer.

*Data of (*M**)*-**15**: ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K, in the presence of 75% of its epimer; recognizable signals): 6.31 (*s*, H–C(10)); 6.30 – 6.15 (H–C(8) and H–C(7); signals covered by those of the epimer); 5.62 (br. *s*, H–C(2)); 4.24 (*dd*, *J* = 3.2 and 1.1, H–C(4)); 2.48 (*sept*, Me_2C*H*–C(9)); 2.00 (*s*, Me–C(6)); 1.86 (*dd*, *J* = 2.2 and 1.4, Me–C(1)); 1.10/1.09 (2*d*, superimp. to *t*, J_{vic} = 6.8, *Me*$_2$CH–C(9)).

Data of **16**: Identical with those reported in [5].

1.1.8. *Dimethyl (*P**,3*S**,4*S**)- and (*M**,3*S**,4*S**)-1,6,10-Trimethyl-3-((phenylsulfonyl)methyl)-3,4-dihydroheptalene-4,5-dicarboxylate ((P*)-* and *(M*)-***12***)) and*

Methyl 1,6,10-Trimethyl-4-((phenylsulfamoyl)acetyl)heptalene-5-carboxylate (**13**). Heptalenediester **11** (1.00 g, 3.21 mmol) was reacted with methyl phenyl sulfone following the standard conditions. Chromatography (silica gel, hexane/AcOEt 3 : 1) gave crude (*P**)/(*M**)-**12** as a colorless oil (0.80 g, 63%) and **13**, after crystallization from AcOEt/hexane 2 :1, in golden yellow needles (0.445 g, 37%).

*Data of (*P**)/(*M**)*-**12**: Mixture of the two epimers in a ratio of 55 : 45. IR (film): 1731*s* and 1700*s* (C=O, ester), 1307*s* and 1152*s* (sulfone). ^{13}C-NMR (75 MHz, $CDCl_3$, 300 K; identified signals, first value for (*P**)-**12**, second for (*M**)-**12**): 171.80/171.57 (MeOO*C*–C(4)); 166.84/165.57 (MeOO*C*–C(5)); 156.94/155.31 (C(5a)); 139.78/139.31 (C_{ip} of $PhSO_2$); 59.74/58.58 (C(1')); 52.03/51.88 (*Me*OOC–C(5)); 51.30/51.22 (*Me*OOC–C(4)); 44.73/44.37 (C(4)); 34.50/33.29 (C(3)).

Data of **13**: M.p. 171 – 172°. ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; C*H*Cl_3 at 7.260): 7.87 (*d* with f.s., H_o of $PhSO_2$); 7.62 (*tt*-like, H_p of $PhSO_2$); 7.51 (*t*, H_m of $PhSO_2$); 7.35 (*dd*-like, ^3J(3,2) = 5.9, ^5J(3, Me–C(1)) = 0.9, H–C(2)); 6.42 (*dd*, ^3J(8,9) = 11.1, ^3J(8,7) = 5.6, H–C(8)); 6.33 (*d*, ^3J(9,8) = 11.1, H–C(9)); 6.32 (*dd*-like, ^3J(2,3) = 5.9, H–C(2)); 6.13 (*d*, ^3J(7,8) = 5.8, H–C(7)); 4.44 (*s*, H_2C(1')); 3.57 (*s*, MeOOC–C(5)); 2.03 (*t*-like, Me–C(6)); 1.97 (*t*-like, Me–C(1)); 1.78 (Me–C(1)). EI-MS: 496 (98, M^+), 295 (40, [*M* – $PhSO_2$]$^+$), 263 (36, [*M* – ($PhSO_2$ + MeOH)]$^+$), 228 (14, [*M* – $PhSO_2CH_2C(O)C{\equiv}CH$]$^+$), 170 (100, [$Me_3C_{10}H_5$]$^+$).

1.1.9. *Dimethyl (*P**,3*S**,4*S**)- and (*M**,3*S**,4*S**)-9-Isopropyl-1,6-dimethyl-3-((morpholinosulfonyl)methyl)-3,4-dihydroheptalene-4,5-dicarboxylate ((*P**)- and (*M**)-**19***) [4]. We used the material prepared in 1996. According to our present analysis, **6a** in [4] represents the (*P**)-epimer as shown by its ^{1}H-NMR (*Table 10* in [4]) and its X-

ray crystal-structure determination [4]. In turn, **6b** in [4] is the corresponding (*M**)-form.

1.1.10. *Dimethyl (*P*,*3*S*,*4*S*)*- and (M*,3S*,4S*)-9-Isopropyl-1,6-dimethyl-3-((*N,N-*diphenylaminosulfonyl)methyl)-3,4-dihydroheptalene-4,5-dicarboxylate* ((*P**)- and (*M**)-**17**)*) and Methyl 9-Isopropyl-1,6-dimethyl-4-((*N,N-*diphenylaminosulfamoyl)-methyl)heptalene-5-carboxylate* (**18**). The standard procedure with *N*,*N*-diphenyl methanesulfonamide (0.740 g, 3.00 mmol) [14] and heptalendiester **14** (0.465 g, 1.36 mmol) gave after workup and chromatography (silica gel, hexane/AcOEt 3 : 1) a 3 :1 mixture of (*P**)- and (*M**)-**17** (0.585 g, 36%) as a yellow-brown oil and **18** (0.186 g, 12%) as a dark brown oil. Both oils were not purified further.

*Data of (*P**)*-**17**: Thermal equilibrium mixture of 75% of (*P**)-**17** and 25% of (*M**)-**17**. IR (film): 1732*s* and 1712*s* (C=O, ester); 1347*s* and 1157*s* (sulfonamide). CI-MS: 605.4 (22, $[M + NH_4]^+$), 588.4 (100, $[M + 1]^+$), 556.4 (39, $[(M + 1) - MeOH]^+$), 419.2 (24, $[(M + 1) - Ph_2N]^+$), 355.3 (54, $[(M + 1) - Ph_2NSO_2]^+$), 256.2 (11, $[iPrMe_2C_{10}H_4COOMe]^+$).

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; in the presence of 25% of the (*M**)-epimer): 7.55 – 7.20 (arom. H of both epimers); 6.38 (*s*, H–C(10)); 6.28 (*d*, ^3J(8,7) = 5.9, H–C(8)); 6.14 (*dd*-like, ^3J(7,8) = 6.6, ^4J(7,Me–C(6)) = 1.4, H–C(7)); 6.11 (*dd*-like, ^3J(2,3) = 5.9, ^4J(2,Me–C(1)) = 1.0, H–C(2)); 4.31 (*dd*, $^2J(H_S,H_R)$ = 14.0, $^3J(H_S,3)$ = 2.0, H_S–C(1')); 3.98 (*d*, ^3J(4,3) = 2.4, H–C(4)); 3.72 (*dd*, partly covered by ester signals, $^2J(H_R,H_S)$ = 14.0, $^3J(H_R,3) \approx 8$, H_R–C(3)); 3.67 (*s*, MeOOC–C(5)); 3.58 (*s*, MeOOC–C(4)); 3.42 (br. *s*, H–C(3)); 2.54 (sept, Me_2CH–C(9)); 1.90 (*s*, Me–C(1)); 1.85 (*t*-like, Σ (^4J(Me–C(6),7) + ^5J(Me–C(6),8)) = 2.4, Me–C(6)); 1.13 and 1.11 (2*d*, J_{vic} = 6.9, Me_2CH–C(9)). ^{13}C-NMR (75 MHz, $CDCl_3$, 300 K; in the presence of 25% of the (*M**)-epimer;

assigned signals): 171.15 (MeOO*C*–C(4)); 167.12 (MeOO*C*–C(5)); 151.83 (C(5a)); 146.72 (C(9)); 141.10 (C_{ip} of Ph); 123.96 (C(8)); 123.10 (C(7)); 120.79 (C(5)); 55.99 (C(1')); 51.71 (*Me*OOC–C(4,5)); 44.80 C(4)); 35.70 (Me_2*C*H–C(9)); 34.62 (C(3)); 25.95 (*Me*–C(1)); 23.14 (*Me*$_2$CH–C(9)); 22.33 (*Me*–C(6)).

*Data of (*M**)*-**17**: ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; in the presence of *ca*. 75% of the (*P**)-epimer; identified signals): 6.32 (H–C(10)); 6.30 – 6.09 (H–C(8) and H–C(7); covered by the signals of the (*P**)-**17**); 5.76 (br. *s*, H–C(2)); 3.76 (s, MeOOC–C(5)); 3.42 (*s*, MeOOC–C(4)); 2.48 (sept, Me_2C*H*–C(9)); 2.02 (Me–C(6)); 1.87 (*t*-like, Σ ^4J(Me–C(1),2) + ^5J(Me–C(1),10) = 2.2, Me–C(1)); 1.11 and 1.09 (2*d*, J_{vic} = 6.9, Me_2CH–C(9)). ^{13}C-NMR (75 MHz, $CDCl_3$, 300 K; in the presence of *ca*. 75% of (*P**)-**17**; assigned signals): 171.33 (MeOO*C*–C(4)); 166.29 (MeOO*C*–C(5)); 151.94 (C(5a)); 145.91 (C(9)); 141.52 (C_{ip} of $PhSO_2$); 124.43 (C(8)); 122.50 (C(7)); 120.00 (C(5)); 57.36 (C(1')); 51.89 (*Me*OOC–C(4,5)); 46.25 (C(4)); 35.94 (Me_2*C*H–C(9)); 35.40 (C(3)); 25.69 (*Me*–C(1)); *Me*$_2$CH–C(9)); 22.62 (*Me*–C(6)).

Data of **18**: ^{1}H-NMR (300 MHz, $CDCl_3$; significant signals only): 6.3 – 6.1 (H–C(2,3,7,8)); 5.85 (*s*, H–C(10)); 4.50 and 4.44 (AB, J_{AB} = 13.9, H_AH_B–C(2')); 2.45 (*sept*, Me_2C*H*–C(9)); 2.07 (*d*-like, ^4J(Me–C(1),2) = 1.1, Me–C(1)); 1.06 and 1.01 (2*d*, J_{vic} = 6.9, *Me*$_2$CH–C(9)). ^{13}C-NMR (75 MHz, $CDCl_3$, 300 K): 188.45 (O=*C*–C(4)); 167.64 (MeOO*C*–C(5)).

1.1.11. *Dimethyl (*P*, *3*S*,*4*S**)-9-Isopropyl-1,6-dimethyl-3-((*R**)1-(phenylsulfonyl)-ethyl)-3,4-dihydroheptalene-4,5-dicarboxylate ((P*)-***23***) and Methyl (*P**)-7-Iso-propyl-1,6-dimethyl-4-((*S**)-2-(phenylsulfonyl)propionyl)heptalene-5-carboxylate* (**24**). See [5] for the X-ray crystal structure of (*P**)-**23**. The ^{1}H- and ^{13}C-NMR spectra

of (*P**)-**23** were again measured and all atom positions fully assigned. Some had to be corrected with respect to those reported in [5]. ^{1}H-NMR (600 MHz, $CDCl_3$, 300 K; C*H*Cl_3 at 7.260): 8.00 (*dd*-like, J_o = 7.3, $J_m \approx$ 1.4, H_o of $PhSO_2$); 7.65 (*tt*, J_o = 7.4, $J_m \approx$ 1.1, H_p of $PhSO_2$); 7.58 (*t*, J_o = 7.7, H_m of $PhSO_2$); 6.32 (*s*, H–C(10)); 6.28 (*d*, ^{3}J(8,7) = 6.5, H–C(8)); 6.14 (*dd*-like, ^{3}J(7,8) = 6.5, ^{4}J(7, Me–C(6)) ≈ 1, H–C(7)); 6.02 (*dd*-like, ^{3}J(2,3) = 5.2, ^{4}J(2,Me–C(1)) ≈ 0.7, H–C(2)); 3.98 (br. *q*, ^{3}J(1',Me–C(1')) = 6.8, ^{3}J(1',3) ≤ 0.6, H–C(1')); 3.97 (*d*, ^{3}J(4,3) = 3.3, H–C(4)); 3.85 (very br., slightly structured *s*, H–C(3)); 3.69 (*s*, MeOOC–C(5)); 3.48 (*s*, MeOOC–C(4)); 2.55 (*sept*, Me_2C*H*–C(9)); 1.96 (*s*, Me–C(6)); 1.95 (*t*-like, ^{4}J(Me–C(1')) ≈ 2·^{5}J(Me–C(1),10) ≈ 1.3, Me–C(1)); 1.31 (*d*, ^{3}J(Me–C(1'),1') = 7.0, Me–C(1')); 1.13/1.09 (2*d*, J_{vic} = 6.9, *Me*$_2$CH–C(9)). ^{13}C-NMR (150 MHz, $CDCl_3$, 300 K; *C*DCl_3 at 77.00): 171.14 (MeOO*C*–C(4)); 167.52 (MeOO*C*–C(5)); 150.31 (C(5a)); 147.10 (C(9)); 138.29 (C_{ip} of $PhSO_2$); 133.98 (C(1)); 133.35 (C_p of $PhSO_2$); 131.81 (C(10a)); 129.14 (C_o of $PhSO_2$); 129.09 (C(6)); 128.95 (C_m of $PhSO_2$); 127.80 (C(2)); 127.08 (C(10)); 123.96 (C(8)); 123.48 (C(7)); 121.32 (C(5)); 59.93 (C(1')); 51.91 (*Me*OOC–C(5)); 51.75 (*Me*OOC–C(4)); 44.71 (C(4)); 36.68 (C(3)); 35.95 (Me_2*C*H–C(9)); 26.54 (*Me*–C(1)); 24.41/22.46 (*Me*$_2$CH–C(9)); 11.25 (*Me*–C(1')).

1.1.11.1. *Dimethyl (*P*,*3*S*,*4*S**)-9-Isopropyl-1,4,6-trimethyl-3-((*S**)-1-phenylsulfonyl)ethyl)-3,4-dihydroheptalene-4,5-dicarboxylate ((P*)-***41***)*. NaH (0.025 g, 1.05 mmol; obtained from an NaH suspension in mineral oil by washing with hexane) in THF (0.5 mL) was cooled to –10°, followed by the addition of (*P**)-**23** (0.425 g, 0.83 mmol, dissolved in THF (3 mL). The mixture was stirred for 4 h without further cooling and then was MeI (0.185 g, 0.08 mL, 1.30 mmol) added. After 3 d stirring at ambient temperature, water was added. The product was extracted with Et_2O and

crystallized from this solvent, which gave (*P**)-**41** in pale yellow crystals (0.420 g, 95%).

*Data of (*P**)*-**41**: M.p. 127 – 128°. IR (KBr): 1740*s* and 1701*s* (C=O, ester), 1325*s* and 1148*s* (sulfone). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): 7.93 (*d* with f.s., $J_o \approx 8$, H_o of $PhSO_2$); 7.56 – 7.47 (superimp. signals of H_p and H_m of $PhSO_2$); 6.35 (*s*, H–C(10)); 6.28 (*d*, ^3J(8,7) = 6.4, H–C(8)); 6.17(*dd*-like, ^3J(2,3) = 6.0, ^4J(2, Me–C(1)) = 1.1, H–C(2)); 6.11 (*dd*-like, ^3J(7,8) = 6.5, ^4J(7,Me–C(6)) = 1.3, H–C(7)); 4.30 (br. *q*, ^3J(1',Me–C(1')) ≈ 6.5, H–C(1')); 3.81 (*s*, MeOOC–C(5)); 3.57 (*s*, MeOOC–C(4)); 3.08 (br. *d*, ^3J(3,2) = 5.5, H–C(3)); 2.58 (*sept*, Me_2CH–C(9)); 2.11 (*s*, Me–C(6)); 2.06 (*s*, Me–C(1)); 1.66 (br. *s*, Me–C(4)); 1.51 (*d*, ^3J(Me–C(1'),1') = 7.0, Me–C(1')); 1.15 (*d*, J_{vic} = 6.9, pro-*R* Me of Me_2CH–C(9)); 1.10 (*d*, J_{vic} = 6.8, pro-*S* Me of Me_2CH–C(9)). Relevant ^{1}H-NOE: pro-*R* Me of Me_2CH–C(9) ⇔ Me–C(4) and H–C(8); pro-*S* Me of Me_2CH–C(9) ⇔ H–C(10); these ^{1}H-NOE prove also the (*P**)-configuration of the 3,4-dihydroheptalene skeleton and the (*S*)-configuration at C(4). ^{13}C-NMR (75 MHz,$CDCl_3$, 300 K): 176.36 MeOO*C*–C(4)); 170.88 (MeOO*C*–C5)); 145.79 (C(9)); 144.94 (C(5a)); 140.92 (C_{ip} of $PhSO_2$); 135.23 (C(1)); 132.64 (C_p of $PhSO_2$); 131.04 (C(6)); 130.74 (C(10a)); 128.77 (C_o of $PhSO_2$); 128.53 (C_m of $PhSO_2$); 127.47 (C(10)); 125.10 C(5)); 124.25 (C(2)); 124.11 (C(8)); 123.22 (C(7)); 61.89 (C(1')); 52.45 (*Me*OOC–C(5)); 52.05 (*Me*OOC–C(4)); 51.62 (C(4)); 50.09 (C(3)); 36.23 (Me_2*C*H–C(9)); 25.59 (*Me*–C(1)); 23.76 and 22.50 (*Me*$_2$CH–C(9)); 23.18 (*Me*–C(6)); 19.36 (*Me*–C(1')). CI-MS: 525.2 (100, $[M + 1]^+$), 493.2 (10, $[(M + 1) - MeOH]^+$), 404.2 (10), 386.2 (16), 286.1 (57), 257.2 (74, $[(iPrMe_2C_{10}H_5COOMe]^+$).

The structure and relative configuration of (*P**)-**41** was finally proved by an X-ray crystal-structure analysis (*cf. Table 7* and *Fig. 4*).

2. Formation of the 3,3-Dimethoxy-5-(1-(phenylsulfonyl)ethyl)-4,5-dihydrohepta-leno[1,2-*c*]furan-1(3*H*)-ones. – 2.1. *General Procedure*. At 0° and under argon and stirring, a solution (1-(phenylsulfonyl)ethyl)lithium in THF (25 mL) is prepared from the sulfone (1.76 mmol) and BuLi (2.5 M in hexane; 2.20 mmol). The solution is than cooled to –78° and the 3,3-dimethoxy-1,3-dihydroheptaleno[4,5-*c*]furan-1-one (1.50 mmol) in THF (5 mL) is added drop by drop. After 3 h stirring at –78°, the mixture is quenched with ice-cooled aq. HCl (17%). After extraction with AcOEt, the AcOEt phase is washed and dried (Na_2SO_4). The residue of the AcOEt phase is then re-crystallized.

2.1.1. *(*P*,5*S*)- and (*M*,5*S*)-8-Isopropyl-3,3-dimethoxy-6,11-dimethyl-5-((*R*)-1-(phenylsulfonyl)ethyl)-4,5-dihydroheptaleno[1,2-*c*]furan-1-(3*H*)-one* ((*P*)- and (*M*)-**27**). Furan-1-one **25** (0.50 g, 1.47 mmol) [7] was reacted with $EtSO_2Ph$ (0.306 g, 1.76 mmol) under the standard conditions and gave, after re-crystallization from Et_2O, (*P*)-**27** in pale yellow crystals (0.625 g, 92%). Dissolution of the crystals in $CDCl_3$ at 243 K showed only the presence of (*P*)-**27** (^{1}H-NMR); at ambient temperature, a 64 : 36 mixture of (*P*)- and (*M*)-**27** was established in a short time.

*Data of (*P*)-***27***: M.p. 158.0 – 160.1°. R_f (AcOEt/hexane 1 : 2) 0.59. IR (KBr): 1768*s* (C=O, five-ring lactone). ^{1}H-NMR (600 MHz, $CDCl_3$, 300 K, in the presence of 36% of (*M*)-**27**; C*H*Cl_3 at 7.264): 7.765 (*dd*-like, J_o = 8.3, J_m = 1.1, H_o of $PhSO_2$); 7.627 (*tt*-like, *J* = 7.5, 1.1, H_p of $PhSO_2$); 7.504 (*t* with f.s., *J* = 7.9, H_m of $PhSO_2$); 6.318 (*dd*, ^3J(9,10) = 11.8, ^4J(9,7) = 1.1, H–C(9)); 6.225 (*d*, ^3J(10,9) = 11.9, H–C(10)); 5.838 (br.

s, H–C(7)); 3.472 (s, $(MeO)_2$–C(3))[17]); 3.409 (br. *dt*-like, $^3J(5,4_R)$ = 12.6, $\Sigma\ ^3J(5,4_S)$ + $^3J(5,1')$ = 4.4, H–C(5)); 3.339 (*qd*, $^3J(1',Me–C(1'))$ = 7.1, $^3J(1',5)$ = 2.4, H–C(1')); 2.842 (*dd*, $^2J(H_S,H_R)$ = 20.0, $^3J(H_S,5)$ = 2.0, H_S–C(4)); 2.458 (*sept*, Me_2CH–C(8)); 2.255 (*dd*, $^2J(H_R,H_S)$ = 20.0, $^3J(H_R,5)$ = 12.5, H_R–C(4); 1.967 (*s*, Me–C(11)); 1.590 (*d*-like, ^5J(Me–C(6),7) ≈ 0.8, Me–C(6)); 1.526 (*d*, ^3J(Me–C(1'),1') = 7.1, Me–C(1')); 1.073/1.062 (2*d*, *t*-like superimp., ^3J = 6.7/6.6, Me_2CH–C(8)). ^{13}C-NMR (150 MHz, $CDCl_3$, 300 K, in the presence of 36% of (*M**)-**27**; *C*DCl_3 at 77.00): 166.27 (C(1)); 158.71 (C(3a)); 144.13 (C(8)); 137.75 (C(11)); 137.47 (C_{ip} of $PhSO_2$); 134.77 (C(6a)); 133.82 (C(10)); 133.52 (C_p of $PhSO_2$); 131.74 (C(9)); 129.35 (C(11b)); 129.11 (C_m of $PhSO_2$); 128.82 (C(6)); 128.67 (C_o of $PhSO_2$); 121.42 (C(7)); 119.47 (C(11a)); 118.46 (C(3)); 59.89 (C(1')); 51.59 (MeO–C(3), pro-*R*); 51.48 (MeO–C(3), pro-*S*); 35.39 (C(5)); 34.37 (Me_2*C*H–C(8)); 24.19 (C(4)); 22.76/22.41 (Me_2CH–C(8)); 22.41 (Me–C(11)); 12.08 (Me–C(6)); 9.99 (Me–C(1')). CI-MS: 533.1 (100, $[M + Na]^+$), 391.1 (15, $[(M + Na) – PhSO_2H]^+$).

*Data of (*M**)*-**27**: ^{1}H-NMR (600 MHz, $CDCl_3$, 300 K, in the presence of 64% of (*P**)-**27**; C*H*Cl_3 at 7.264): 7.726 (*dd*-like, J_o = 8.3, J_m = 1.1, H_o of $PhSO_2$); 7.583 (*tt*-like, J = 7.5, 1.1, H_p of $PhSO_2$); 7.463 (*t* with f.s., *J* = 7.9, H_m of $PhSO_2$); 6.456 (*dd*, ^3J(9,10) = 11.8, ^4J(9,7) = 1.1, H–C(9)); 6.365 (*d*, ^3J(10,9) = 11.8, H–C(10)); 5.744 (br. *s*, H–C(7)); 3.783 (*qd*, $^3J(1',Me–C(1'))$ = 7.2, $^3J(1',5)$ = 9.5, H–C(1')); 3.460 (*s*, MeO–C(3), pro-*R*); 3.290 (*s*, MeO–C(3), pro-*S*); 3.783 (*ddd*, $\Sigma\ ^3J(5,4_R)$ + $^3J(5,4_S)$ + $^3J(5,1')$ = 17.9, H–C(5)); 2.656 (*dd*, $^2J(H_R,H_S)$ = 21.0, $^3J(H_R,5)$ = 3.4, H_R–C(4); 2.523 (*dd*, $^2J(H_S,H_R)$ = 21.0, $^3J(H_S,5)$ = 4.6, H_S–C(4)); 2.469 (*sept*, Me_2C*H*–C(8)); 1.930 (*s*, Me–

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[17]) At 243 K, one finds two *s* at 3.458 and 3.425, corresponding presumably to the pro-*R* and pro-*S* group, respectively.

C(11)); 1.599 (*d*, ^5J(Me–C(6),7) = 1.0, Me–C(6)); 1.231 (*d*, ^3J(Me–C(1'),1') = 7.2, Me–C(1')); 1.108/1.090 (2*d*, ^3J = 6.9/6.8, Me_2CH–C(8)). ^{13}C-NMR (150 MHz, $CDCl_3$, 300 K, in the presence of 36% of (*P**)-**27**; *C*DCl_3 at 77.00): 166.12 (C(1)); 157.67 (C(3a)); 143.55 (C(8)); 138.53 (C_{ip} of $PhSO_2$); 137.72 (C(11)); 133.63 (C(9)); 133.34 (C_p of $PhSO_2$); 133.20 (C(10)); 133.10 (C(6)); 131.79 (C(6a)); 129.35 (C_m of $PhSO_2$); 128.88 (C(11b)); 128.67 (C_o of $PhSO_2$); 122.76 (C(7)); 120.33 (C(11a)); 118.08 (C(3)); 60.91 (C(1')); 51.68 (MeO–C(3), pro-*R*); 51.51 (MeO–C(3), pro-*S*); 39.81 (C(5)); 34.31 (Me_2*C*H–C(8)); 25.58 (C(4)); 22.77/22.69 (Me_2CH–C(8)); 22.54 (Me–C(11)); 18.81 (Me–C(6)); 12.76 (Me–C(1')).

2.1.2. *(*P**,5*S**)-3,3-Dimethoxy-7,9,11-trimethyl-5-((*R**)-1-(phenylsulfonyl)ethyl)-4,5-dihydroheptaleno[1,2-*c*]furan-1(3*H*)-one* ((*P**)-**30**). Furanone **28** (0.50 g, 1.60 mmol)[18]) in THF (5 mL) was reacted with $EtSO_2Ph$ (0.327 g, 1.92 mmol) in THF (20 mL) as described. Working up followed by chromatography on silica gel (hexane/ AcOEt 3 : 1) and crystallization from AcOEt/hexane gave pure (*P**)-**30** in pale yellow crystals (0.530 g, 69%).

*Data of (*P**)*-**30**: M.p. 196.3 – 197.3°. R_f (hexane/AcOEt 3 : 2) 0.49. IR (KBr): 1766*s* (C=O, five-ring lactone). ^{1}H-NMR (500 MHz, $CDCl_3$, 300 K; C*H*Cl_3 at 7.264): 7.803 (*d* with f.s., J_o = 7.3, H_o of $PhSO_2$); 7.640 (*t*, J_o = 7.5, H_p of $PhSO_2$); 7.520 (*t*, J_o = 7.8, H_m of $PhSO_2$); 6.124 (br. *s*, H–C(10)); 5.880 (br. *s*, H–C(8)); 5.342 (*d*, ^3J(6,5) = 6.8, H–C(6)); 3.442 (*s*, MeO–C(3), pro-*R*); 3.338 (*s*, MeO–C(3), pro-*S*); 3.26 – 3.19

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[18]) The semi-orthoanhydride **28** (m.p. 118.0 – 119.0° (Et_2O/hexane)) was prepared from the corresponding heptalene half-ester in the described manner [7] (for spectral details see [12]).

(superimp. signals of H–C(1') and H–C(5)); 2.923 (*dd*, $^2J(H_S,H_R)$ = 20.2, $^3J(H_S,5)$ = 2.8, H_S–C(4)); 2.318 (*dd*, $^2J(H_R,H_S)$ = 20.2, $^3J(H_R,5)$ = 12.4, H_R–C(4)); 2.004 (*s*, Me–C(9)); 1.984 (*s*, Me–C(7)); 1.960 (*s*, Me–C(11)); 1.372 (*d*, ^3J(Me–C(1'),1') = 6.9, Me–C(1')). ^{1}H-NMR (600 MHz, [$^2H_6$]acetone, 300 K): 7.74 H_o of $PhSO_2$); 7.64 (H_p of $PhSO_2$); 7.53 (H_m of $PhSO_2$); 6.04 (br. *s*, H–C(10)); 5.80 (*t*-like, $J \approx 1.2$, H–C(8)); 5.43 (*d*, ^3J(6,5) = 7.2, H–C(6)); 3.34 (*qd*, ^3J(1', Me–C(1') = 7.2, ^3J(1',5) ≈ 3.6, H–C(1')); 3.31 (*s*, MeO–C(3), pro-*R*); 3.18 (*s*, MeO–C(3), pro-*S*); 3.06 (*dquint*, $^3J(5,H_R)$ = 12.6, ^3J(5,6) = 7.2, $^3J(5,H_S) \approx {}^3J$(5,1') ≈ 3.3–3.6, H–C(5)); 2.81 (*dd*, $^2J(H_S,H_R)$ = 20.4, $^3J(H_S,5)$ = 3.6, H_S–C(4)); 2.28 (*dd*, $^2J(H_R,H_S)$ = 20.4, $^3J(H_R,5)$ = 12.6, H_R–C(4)); 1.86 (*d*-like, $^4J \approx 1$, Me–C(9)); 1.85 (*d*-like, $^4J \approx 1$, Me–C(7)); 1.78 (*s*, Me–C(11)); 1.24 (*d*, ^3J(Me–C(1'),1') = 7.2, Me–C(1')). ^{13}C-NMR (125 MHz, $CDCl_3$, 300 K; *C*DCl_3 at 77.00): 166.43 (C(1)); 157.48 (C(3a)); 144.66 (C(6a)); 139.55 (C(9)); 139.29 (C(11)); 137.78 (C_{ip} of $PhSO_2$); 136.35 (C(7)); 133.68 (C_p of $PhSO_2$); 129.95 (C(10)); 129.09 (C_m of $PhSO_2$); 128.92 (C(11b)); 128.78 (C_o of $PhSO_2$); 126.66 (C(8)); 123.52 (C(6)); 118.49 (C(3)); 113.61 (C(11a)); 62.49 (C(1')); 51.59 (MeO–C(3), pro-*R*); 51.27 (MeO–C(3), pro-*S*); 33.25 (C(5)); 25.91 (C(4)); 25.60 (Me-C(9)); 24.72 (Me–C(7)); 23.28 (Me–C(11)); 10.41 (Me–C(1')). CI-MS: 505.1 (100, [*M* + Na]$^+$), 363.1 (6, [(*M* + Na) – $PhSO_2H$]$^+$).

The relative configuration of (*P**)-**30** was established by an X-ray crystal-structure analysis (see Fig. X and Table 7).

Heating of pure (*P**)-**30** in $CDCl_3$ at 45° gave after 2 h about 10% of *(*P*,*5*S*)-3,3-dimethoxy-7,9,11-trimethyl-5-((*S*)-1-(phenylsulfonyl)ethyl)-4,5-dihydroheptaleno-[1,2-*c*]furan-1(3*H*)-one*, and, after further heating for 6 h at 45°, a 2 : 1 ratio of (*P**)-**30** and its C(1')-epimer. Epimerization at the heptalene axis of chirality was not

observed. Moreover, heating of pure (*P**)-**30** in [$^2H_6$]acetone at 45° (4 h) left the compound unchanged.

*Data of (*P*,*5*S**)-3,3-dimethoxy-7,9,11-trimethyl-5-((*S**)-1-(phenylsulfonyl)ethyl)-4,5-dihydroheptaleno[1,2-*c*]furan-1(3*H*)-one*: ^{1}H-NMR (600 MHz, $CDCl_3$, 300 K, in the presence of 66% of (*P**)-**30**; C*H*Cl_3 at 7.264): 7.83 (*d*, H_o of $PhSO_2$); 7.65 (*t*, H_p of $PhSO_2$); (*t*, H_m of $PhSO_2$); 6.18 (*s*, H–C(10)); 5.92 (*s*, H–C(8)); 5.41 (*d*, ^3J(6,5) = 7.2, H–C(6)); 3.44 (*s*, MeO–C(3), pro-*R*); 3.34 (*s*, MeO–C(3), pro-*S*); 3.25 – 3.18 (*m*, H–C(1') and H–C(5) of (*P**)- and (*M**)-form); 2.52 (*dd*, $^2J(H_R,H_S)$ = 20.3, $^3J(H_R,5)$ = 12.5, H_R–C(4)); 2.36 – 2.29 (H_S–C(4), covered by H_R–C(4) of (*P**)-form); 2.03 (*s*, Me–C(9)); 2.02 (*s*, Me–C(7)); 2.01 (*s*, Me–C(11)); 1.37 (*d*, ^3J(Me–C(1'),1') = 7.1, Me–C(1')).

2.1.3. *(*P*,*5*R**)-3,3-Dimethoxy-6,7,9,11-tetramethyl-5-((S*)-1-(phenylsulfonyl)ethyl)-4,5-dihydroheptaleno[1,2-c]furan-1-one* ((*P**)-**31**). Furanone **29** (0.180 g, 0.55 mmol) [7] in THF (5 mL) was reacted with $EtSO_2Ph$ (0.204 g, 1.20 mmol) in THF (10 mL) as described. Workup followed by chromatography on silica gel (hexane/AcOEt 5 : 2) and crystallization from AcOEt/hexane gave pure (*P**)-**31** in pale yellow crystals (0.378 g, 64%).

*Data of (*P*)-**31**: M.p. 211.9 – 212.4°. R_f (hexane/AcOEt 3 : 1) 0.34. IR (KBr): 1775*s* (C=O, five-ring lactone). ^{1}H-NMR (500 MHz, $CDCl_3$, 300 K; C*H*Cl_3 at 7.263): 7.734 (*d* with f.s., J_o = 8.2, H_o of $PhSO_2$); 7.610 (*tt*, J_o = 7.5, J_m = 1.2, H_p of $PhSO_2$); 7.495 (*t* with f.s., J_o = 7.5, H_m of $PhSO_2$); 6.165 (br. *s*, H–C(10)); 5.948 (br. *s*, H–C(8)); 3.749 (*qd*, ^3J(1',5) = 9.3, ^3J(1',Me–C(1')) = 7.2, H–C(1')); 3.489 (*s*, MeO–C(3), pro-*R*); 3.236 (*s*, MeO–C(3), pro-*S*); ; 2.922 (*ddd*, $\Sigma\ ^3J(5,4_R) + {}^3J(5,4_S) + {}^3J(5,1')$ = 17.4, H–C(5)); 2.677 (*dd*, $^2J(H_S,H_R)$ = 21.0, $^3J(H_S,5)$ = 3.5, H_S–C(4)); 2.517 (*dd*, $^2J(H_R,H_S)$ = 21.0, $^3J(H_R,5)$ = 4.6, H_R–C(4)); 2.083 (*d*, ^4J(Me–C(9),10) = 0.9, Me–C(9)); 1.893 (*d*,

^{4}J(Me–C(7),8) = 1.2, Me–C(7)); 1.885 (*s*, Me–C(11)); 1.694 (*s*, Me–C(6)); 1.200 (*d*, ^{3}J(Me–C(1'),1') = 7.2, Me–C(1')). ^{13}C-NMR (125 MHz, $CDCl_3$, 300 K; *C*DCl_3 at 77.00): 166.17 (C(1)); 157.49 (C(3a)); 141.23 (C(9)); 138.44 (C_{ip} of $PhSO_2$); 136.78 (C(11)); 135.84 (C(7)); 133.42 (C_p of $PhSO_2$); 132.63 (C(6a)); 132.57 (C(6)); 129.55 (C(10)); 128.83 (C_m of $PhSO_2$); 128.64 (C(11b)); 128.60 (C_o of $PhSO_2$); 126.78 (C(8)); 118.24 (C(3)); 115.91 (C(11a)); 61.31 (C(1')); 51.58 (MeO–C(3), pro-*R*); 51.23 (MeO–C(3), pro-*S*); 39.29 (C(5)); 26.27 (C(4)); 25.11 (Me-C(9)); 22.70 (Me–C(7)); 21.93 (Me–C(11)); 19.90 (Me–C(6)); 13.21 (Me–C(1')). CI-MS: 519.1 (100, $[M + Na]^+$), 377.2 (7, $[(M + Na) – PhSO_2H]^+$).

The relative configuration of (*P**)-**31** was established by an X-ray crystal-structure determination (see Fig. X and Table Y).

2.1.4. *Methyl* 8-(*tert-Butyl)-1-methyl-5-(2-(phenylsulfonyl)propanoyl)heptalene-4-carboxylate* (**33**) and *(*P*,*5*S**)-9-(*tert-*Butyl)-3,3-dimethoxy-6-methyl-5-((*R**)-1-(phenylsulfonyl)ethyl)-4,5-dihydroheptaleno[1,2-*c*]furan-1-one* ((*P**)-**34**). Furanone **32** (0.340 g, 1.00 mmol)[19]) in THF (5 mL) was reacted in the usual manner with $EtSO_2Ph$ (0.204 g, 1.20 mmol) in THF (10 mL). Workup followed by chromatography on silica gel (hexane/AcOEt 5 : 2) gave after crystallization from Et_2O/hexane **33** (0.378 g, 79%) as an orange crystal powder. (*P**)-**34** could be enriched (in total <5 %) in the mother liquor.

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[19]) The semi-orthoanhydride **32** (m.p. 162.0 – 163.0° (Et_2O/hexane)) was prepared from the corresponding heptalene half-ester in the described manner [7] (for spectral details see [13]).

Data of **33**: M.p. 136.5 – 140.5°. R_f (hexane/AcOEt 5 : 2) 0.28. The compound formed in $CDCl_3$ solution a 3 : 1 mixture, presumably of the (*P**)- and (*M**)-epimers, with unknown relative configuration of the 2-(phenylsulfonyl)propanoyl substituent at C(5). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; major epimer): 7.84 (*d*, J_o = 7.4, H_o of $PhSO_2$); 7.66 (*t*-like, H_p of $PhSO_2$); 7.55 (*t*-like, H_m of $PhSO_2$); 7.47 (*d*, ^3J(3,2) = 6.2, H–C(3)); 6.39 (*d*, ^3J(9,10) = 7.0, H–C(9)); 6.38 (*d*, ^3J(7,6) = 11.5, H–C(7)); 6.02 (*d*, ^3J(6,7) = 11.5, H–C(6)); 5.91 (superimp. *d*, ^3J = 7.0, H–C(2,10)); 4.11 (*q*, ^3J = 6.9, H–C(2')); 3.71 (*s*, *Me*OOC–C(4)); 2.00 (*s*, Me–C(1)); 1.46 (*d*, ^3J = 6.9, Me–C(2')); 1.16 (*s*, Me_3C–C(8)). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; minor epimer): 7.99 (*d*, J_o = 7.6, H_o of $PhSO_2$); 7.64 (*t*-like, H_p of $PhSO_2$); 7.54 (*t*-like, H_m of $PhSO_2$); 7.38 (*d*, ^3J(3,2) = 6.3, H–C(3)); 6.73 (*d*, ^3J(7,6) = 11.2, H–C(7)); 6.56 (*d*, ^3J(9,10) = 6.6, H–C(9)); 6.29 (*d*, ^3J(6,7) = 11.2, H–C(6)); 6.09 (*d* with f.s., ^3J(2,3) = 6.3, H–C(2)); 6.00 (*d*, ^3J(10,9) = 7, H–C(10)); 4.87 (*q*, ^3J = 6.8, H–C(2')); 3.55 (*s*, *Me*OOC–C(4)); 2.03 (*s*, Me–C(1)); 1.46 (*d*, ^3J = 6.9, Me–C(2')); 1.20 (*s*, Me_3C–C(8)). ^{13}C-NMR (75 MHz, $CDCl_3$, 300 K; major epimer): 191.41 (C(1')); 167.49 (MeOO*C*–C(4)); 154.70 (C(8)); 146.46 (C(1)); 143.85 (C(3)); 143.76 (C(5a)); 137.92 (C_{ip} of $PhSO_2$); 133.69 (C_p of $PhSO_2$); 133.50 (C(10a)); 132.61 (C(4)); 131.07 (C(7)); 129.00 (C_o of $PhSO_2$); 128.86 (C(10)); 128.62 (C_m of $PhSO_2$); 124.31 (C(9)); 125.88 (C(2)); 123.90 (C(6)); 122.10 (C(5)); 68.86 (C(2')); 52.28 (*Me*OOC–C(4)); 36.23 Me_3*C*–C(8)); 29.90 (Me_3C–C(8)); 26.37 (Me–C(1)); 11.91 (Me–C(2')).

*Data of (*P**)*-**34**: Enrichment *ca*. 80 %. Relative configuration in analogy to (*P**)-**27** and (*P**)-**31** presumably (*P**,1'*S**,5*R**). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): 7.81 (*d*-like, $J_o \approx 7.1$, H_o of $PhSO_2$); 7.66 (*t*-like, $J_o \approx 7.3$, H_p of $PhSO_2$); 7.56 (*t*-like, H_m of $PhSO_2$); 6.91 (*d*, ^3J(10,11) = 7.1, H–C(10)); 6.29 (*d*, ^3J(11,10) = 7.1, H–C(11)); 6.24 (*dd*-like, ^3J(7,8) = 11.3, ^5J(7,Me–C(6)) ≈ 1.6, H–C(7)); 5.90 (*d*, ^3J(8,7) = 11.3, H–

C(8)); 3.53 (*s*, MeO–C(3), pro-*R*); 3.45 (s, MeO–C(3), pro-*S*); 3.60 – 3.40 (superimp. signals of H–C(1') and H_S–C(4)); 2.90 (*dt*-like, $^3J(5,H_S) \approx 10.8$, H–C(5)); 2.74 (*dd*, $^2J(H_R,H_S) = 20.7$, $^3J(H_R,5) = 3.6$, H_R–C(4)); 1.75 (*d*, ^5J(Me–C(6),7) ≈ 1.1, Me–C(6)); 1.10 (*s*, Me_3C–C(9)); 0.93 (*d*, $^3J = 7.0$, Me–C(1')). ^{13}C-NMR (75 MHz, $CDCl_3$, 300 K; some assignments are tentative): 167.46 (C(1)); 154.59 (C(9)); 154.33 (C(3a)); 137.49 (C_{ip} of $PhSO_2$); 133.60 (C_p of $PhSO_2$); 129.05 (C_m of $PhSO_2$); 128.80 (C_o of $PhSO_2$); 127.95 (C(8)); 126.49 (C(11); 126.40 (C(10)); 122.04 (C(7)); 118.51 (C(3)); residual signals in the range of 150 – 120 not assignable; 59.46 (C(1')); 51.92 (MeO–C(3), pro-*R*); 51.48 (MeO–C(3), pro-*S*); 42.03 (C(5)); 35.48 (Me_3C–C(9)); 29.83 (Me_3C–C(9)); 21.24 (Me–C(6)); 13.86 (Me–C(1')).

3. Formation of the Alkylated Dimethyl Heptalene-4,5- and -1,2-dicarboxylates by Base-Catalyzed Elimination of Benzenesulfinic Acid from the Corresponding Sulfones. – 3.1. *Standard Procedure*. Sodium methoxide (2.2 mmol) is freshly prepared from Na in MeOH (3 mL). The sulfone (2.2 mmol) is added in THF (3 mL) and the mixture heated at reflux for 3 to 12 h. Then, after cooling, aq. 1N HCl is added and the mixture extracted with Et_2O. The thus obtained dimethyl heptalenedicarboxylate, in some cases accompanied by the corresponding cyclic anhydride, is purified by chromatography on silica gel.

3.1.1. *Dimethyl 3-Methylheptalene-4,5-dicarboxylate (***36***) and Dimethyl 3-Methylheptalene-4,5-dicarboxylic anhydride (*4-methylheptaleno[4,5-*c*]furan-1,3-dione; **43***)*. 3.1.1.1. With MeONa/MeOH: Sulfone (*P**)/(*M**)-**2** (0.150 g, 0.352 mmol) was heated for 12 h under the standard conditions and then worked up, which gave mainly **43** (0.045 g, 54%) as a dark red oil and only trace amounts (< 2%) of **36**.

Data of **43**: IR (film): 1790.5*s* and 1740*s* (C=O, 5-ring anhydride). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; C*H*Cl_3 at 7.260): 6.60 (*d*, ^{3}J(6,7) = 11.4, H–C(6)); 6.45 (*dd*, ^{3}J(9,8) = 10.8, ^{3}J(9,10) = 7.6, H–C(9)); 6.37 (*ddd*, ^{3}J(7,6) = 11.4, ^{3}J(7,8) = 7.1, ^{4}J(7,9) = 1.1, H–C(7)); 6.21 (*ddd*, ^{3}J(8,9) = 10.8, ^{3}J(8,7) = 7.1, ^{4}J(8,6) = 0.7, H–C(8)); 5.76 (*d*, ^{3}J(1,2) = 11.4, H–C(1)); 5.48 (*d*, ^{3}J(10,9) = 7.6, H–C(10)); 5.33 (d, 3J(2,1) = 11.3, H–C(2)); 2.36 (*s*, Me–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$, 300 K; $CDCl_3$ at 77.00): 163.75 and 160.22 (C=O, 5-ring anhydride); 151.05; 148.58; 139.09; 137.92; 136.52; 135.92; 135.73; 135.25; 133.58; 128.80; 126.47; 118.94; 20.85 (Me–C(3)). EI-MS: 238 (55, M^+), 181 (20), 165 (25), 153 (30); 134 (25); 109 (65), 95 (100).

3.1.1.2. With *t*-BuOK: Sulfone (*P**)/(*M**)-**2** (0.150 g, 0.352 mmol) was dissolved in THF (3 mL) and *t*-BuOK (0.080 g, 0.69 mmol) in THF (1 mL) was added. After 2 h stirring at ambient temperature, work up was performed under the standard condition to yield **36** as orange colored oil (0.031 g, 31%).

Data of **36**: ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): 6.50 – 5.70 (*m*, 7 H); 2.26 (s, Me–C(3)). EI-MS: 284 (52, M^+), 186 (100, [*M* – MeC≡CCOOMe]$^+$).

3.1.2. *Dimethyl 1,3,6-Trimethylheptalene-4,5-dicarboxylate (***38***) and Dimethyl 3,5,10-Trimethylheptalene-1,2-dicarboxylate (***38'***)*. Sulfone (*P**)-**10** (0.060 g, 0.132 mmol) was reacted for 12 h and then worked up under the standard conditions to yield a thermally equilibrated 2 : 1 mixture of **38** and **38'** (0.027 g, 66%) as a dark yellow oil. IR (film): 1726*s* and 1709*s* (C=O, ester). EI-MS: 312 (90, M^+), 297 (77, [*M* – Me]$^+$), 214 (100, [*M* – MeC≡CCOOMe]$^+$).

Data of **38**: ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; 67% in the mixture of DBS isomers): *ca*. 6.49 (^3J = 6.5, H–C(7,10)); *ca*. 6.21 (signals superimp. with those of H–C(7) of **38'**, H–C(8) or H–C(9)); 6.01 (*d*-like, ^4J(2,Me–C(1)) = 1.4, H–C(2)); *ca*. 5.95 (signals superimp. with those of H–C(6) of **38'**, H–C(9) or H–C(8)); 3.68 (*s*, MeOOC-C(5)); 3.62 (*s*, MeOOC–C(4)); 2.26 (*s*, Me–C(3)); 2.03 (*d*, ^4J(Me–C(1),2) = 1.3, Me–C(1)); 2.00 (*d*, ^4J(Me–C(6),7) = 1.4, Me–C(6)).

Data of **38'**: ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; 33% in the mixture of DBS isomers): 6.43 (*s*, H–C(4)); 6.42 (*d*, ^3J(9,8) = 11.4, H–C(9)); 6.38 (*dd*, ^3J(8,9) = 11.3, ^3J(8,7) = 5.6, H–C(8)); 6.22 (*dd*, partly covered by signals of **38**, ^3J(7,8) = 5.6, H–C(7)); *ca*. 5.95 (*d*, mostly covered by signals of **38**, ^3J(6,7) ≈ 11, H–C(6)); 3.90 (*s*, MeOOC-C(5)); 3.66 (*s*, MeOOC–C(4)); 2.01 (*d*, ^4J(Me–C(3),4 = 1.2, Me–C(3)); 1.75 (*s*, Me–C(10)); 1.67 (*s*, Me–C(5)).

3.1.2. *Dimethyl 1,3,6,10-Tetramethylheptalene-4,5-dicarboxylate (***39***) and Dimethyl 3,5,6,10-Tetramethylheptalene-1,2-dicarboxylate (***39'***)*. Sulfone (*P**)/(*M**)-**12** (0.100 g, 0.229 mmol) was reacted for 12 h and then worked up under the standard conditions. The thermally equilibrated 2 : 1 mixture of **39** and **39'** was separated by TLC on silica gel (hexane/Et_2O 4 : 1) to give , after crystallization from Et_2O/hexane 1 : 4, pure **39** (0.013 g, 18%) and pure **39'** (0.007 g, 9%).

Data of **39**: M.p. 145 – 146°. IR (KBr): 1724*s* and 1704*s* (C=O, ester). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; $CHCl_3$ at 7.260): 6.44 (*dd*, ^3J(8,9) = 11.3, ^3J(8,7) = 6.0, H–C(8)); 6.37 (*d*, ^3J(9,8) = 11.3, H–C(9)); 6.13 (*dd*-like, ^3J(7,8) = 5.8, H–C(7)); 6.09 (*d*-like, ^4J(2,Me–C(1)) = 1.4, H–C(2)); 3.66 (*s*, MeOOC–C(5)); 3.60 (*s*, MeOOC–C(4)); 2.27 (*s*, Me–C(3)); 1.98 (*t*-like, ^4J(Me–C(6),7) ≈ 2 × ^5J(Me–C(6),8) = 1.3, Me–C(6)); 1.94

(*d*, ^4J(Me–C(1),2) = 1.4, Me–C(1)); 1.79 (*s*, Me–C(10)). ^{13}C-NMR (75 MHz, $CDCl_3$, 300 K; $CDCl_3$ at 77.00): 168.10 (MeOO*C*–C(4)); 167.45 (MeOO*C*–C(5)); 148.03 (C(3)); 147.00 (C(5a)); 140.07 (C(6)); 132.72 (C(8)); 132.11 (C(9)); 131.69 (C(1)); 130.20 (C(7)); 129.20 (C(10)); 127.48 (C(4)); 126.94 (C(10a)); 124.49 (C(2)); 122.78 (C(5)); 51.78 (*Me*OOC–C(5)); 51.46 (*Me*OOC–C(4)); 22.70 (Me–C(1)); 22.25/22.13 (Me–C(6,10)); 18.07 (Me–C(3)). EI-MS: 326 (79, M^+), 311 (60, [M – Me]$^+$), 267 (31, [M – COOMe]$^+$), 252 (24, [M – (COOMe + Me)]$^+$), 228 (100, [M – MeC≡CCOOMe]$^+$).

Data of **39'**: M.p. 131 – 132°. ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K; $CHCl_3$ at 7.260): 6.45 (*d*-like, ^4J(4,Me–C(3)) = 1.2, H–C(4)); 6.32 (*dd*, ^3J(8,9) = 11.1, ^3J(8,7) = 6.3, H–C(8)); 6.30 (*d*, ^3J(9,8) = 11.1, H–C(9)); 6.15 (*dd*-like, ^3J(7,8) = 6.3, ^4J(7,Me–C(6)) ≈ 1.5, H–C(7)); 3.69 (*s*, MeOOC–C(5)); 3.67 (*s*, MeOOC–C(4)); 2.03 (*d*, ^4J(Me–C(3),4) = 1.2, Me–C(3)); 1.99 (*d*, ^4J(Me–C(6),7) = 1.5, Me–C(6)); 1.76 (*s*, Me–C(10)); 1.67 (s, Me–C(5)). EI-MS: 326 (100, M^+), 311 (94, [M – Me]$^+$), 295 (22, [M – MeO]$^+$), 267 (18, [M – COOMe]$^+$), 252 (35, [M – (COOMe + Me]$^+$), 228 (73, [M – MeC≡CCOOMe]$^+$).

3.1.4. *Dimethyl 9-Isopropyl-1,3,6-trimethylheptalene-4,5-dicarboxylate (***35***), Dimethyl 7-Isopropyl-3,5,10-trimethylheptalene-1,2-dicarboxylate (***35'***), and 9-Isopropyl-1,3,6-trimethyl-4,5-dicarboxylic Anhydride* (8-isopropyl-4,6,11-trimethyl-heptaleno[4,5-*c*]furan-1,3-dione; **44**). 3.1.4.1. With MeONa/MeOH: Following the standard procedure, sulfone (*P**)-**15** (0.080 g, 0.161 mmol) yielded after 12 h a 3 : 2 mixture of **35** and **35'** (0.022 g, 39%) (*cf.* [9]).

Data of **35**: M.p., UV, and IR, see [9]. We report here again the ^{1}H-NMR since the locants of the heptalene skeleton had been reversed in the meantime according to the IUPAC rules (C(5) old → C(1) new, *etc*.), and some atomic positions of **35** and of **35'** had to be reassigned according to our new full ^{1}H,^{13}C analysis. ^{1}H-NMR (600 MHz, $CDCl_3$, 300 K, C*H*Cl_3 at 7.270; 60% of **35**): 6.291 (*d*, ^3J(8,7) = 6.6, H–C(8)); 6.134 (*dd*-like, ^3J(7,8) = 6.5, ^4J(7,Me–C(6)) = 1.0, H–C(7)); 6.006 (*d*-like, ^4J(2,Me–C(1)) = 1.2, H–C(2)); 5.862 (*s*, H–C(10)); 3.685 (*s*, MeOOC–C(5)); 3.625 (*s*, MeOOC–C(4)); 2.500 (*sept*, Me_2C*H*–C(9)); 2.269 (*s*, Me–C(3)); 2.019 (d, 4J(Me–C(1),2) = 1.3, Me–C(1)); 2.003 (*s*, Me–C(6)); 1.102 and 1.069 (2*d*, J_{vic} = 6.9 and 6.8, Me_2CH–C(9)). 13C-NMR (150 MHz, $CDCl_3$, 300 K, *C*DCl_3 at 77.00; 60% of **35**): 168.12 (MeOO*C*-C(4)); 167.74 (MeOO*C*–C(5)); 148.27 (C(3)); 148.10 (C(9)); 145.71 (C(5a)); 141.31 (C(1)); 131.70 (C(2)); 131.39 (C(10a)); 128.81 (C6)); 127.91 (C(4)); 126.10 (C(7)); 125.07 (C(8)); 124.39 (C(10)); 123.16 (C(5)); 51.89 (*Me*OOC–C(5)); 51.45 (*Me*OOC–C(4)); 35.58 (Me_2*C*H–C(9)); 25.11 (Me–C(1)); 22.98 and 22.59 (*Me*$_2$CH-C(9)); 22.71 (Me–C(3)); 22.57 (Me–C(6)). GC-MS: 354 (60, M^+), 339 (50, [*M* – Me]$^+$), 295 (10, [*M* – COOMe]$^+$), 256 (100, [*M* – MeC≡CCOOMe]$^+$).

Data of **35'**: ^{1}H-NMR (600 MHz, $CDCl_3$, 300 K, C*H*Cl_3 at 7.270; 40% of **35'**; see also [9]): 6.438 (br. *s*, H–C(4)); 6.378 (*d*, ^3J(9,8) = 11.9, H–C(9)); 6.345 (*dd*-like, ^{3}J(8,9) = 11.9, ^4J(8,6) ≈ 1.0, H–C(8)); 5.730 (*s*, H–C(6)); 3.878 (*s*, MeOOC–C(5)); 3.658 (*s*, MeOOC–C(4)); 2.543 (*sept*, Me_2C*H*–C(7)); 2.008 (*d*, ^4J(Me–C(5),4) = 1.1, Me–C(5)); 1.746 (*s*, Me–C(3)); 1.652 (*s*, Me–C(10)); 1.134 and 1.127 (2*d*, J_{vic} = 6.9 and 6.8, *Me*$_2$CH–C(7)). ^{13}C-NMR (150 MHz, $CDCl_3$, 300 K, $CDCl_3$ at 77.00; 40 % of **35'**): 168.90 (MeOOC–C(5)); 165.43 (MeOOC–C(4)); 148.40 (C(7)); 146.06 (C(5a)); 138.89 (C(4)); 135.51 (C9)); 135.48 (C(2)); 132.96 (C(10)); 132.90 (C(5)); 131.98 (C(8)); 129.67 (C(3)); 127.50 (C(10a)); 121.83 (C(6)); 120.52 (C(1)); 52.41

(MeOOC–C(5)); 52.29 (MeOOC–C(4)); 34.84 (Me_2*C*H–C(7)); 22.88 and 22.63 (*Me*$_2$CH–C(7)); 22.48 (Me–C(5)); 17.37 (Me–C(10)); 17.15 (Me–C(3)).

3.1.4.2. With *t*-BuOK: Treatment of sulfone (*P**)-**12** (0.130 g, 0.262 mmol) according to 3.1.1.2 gave after chromatographic separation on silica gel (hexane/AcOEt 2 : 1) a 3 : 2 mixture of **35** and **35'** (0.021 g, 23%) and, after crystallization from AcOEt/hexane 1 : 2, orange colored crystals of **44** (0.016 g, 20%).

Data of **44**: M.p. 141 – 142°. IR (KBr): 1806*s* and 1754*s* (5-ring anhydride). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): 6.40 (*dd*-like, ^3J(7,8) = 7.0, ^4J(7,Me–C(6)) = 1.3, H–C(7)); 6.26 (*d*, ^3J(8,7) = 7.0, H–C(8)); 6.17 (br. *s*, H–C(2)); 5.93 (*s*, H–C(10)); 2.49 (sept, partly covered by signal of Me–C(3), Me_2C*H*–C(9)); 2.45 (*s*, Me–C(3)); 2.29 (s, Me–C(1)); 2.17 (*s*, Me–C(6)); 1.10 and 1.08 (2*d*, J_{vic} = 6.7 and 6.6, *Me*$_2$CH–C(9). CI-MS: 326.2 (100, $[M + NH_4]^+$), 309.2 (80, $[M + 1]^+$).

3.1.5. *Dimethyl 3-Ethyl-9-isopropyl-1,6-dimethylheptalene-4,5-dicarboxylate (***40***) and Dimethyl 3-Ethyl-7-isopropyl-5,10-dimethylheptalene-1,2-dicarboxylate (***40'***)*. Sulfone (*P**)/(*M**)-**23** (0.200 g, 0.392 mmol) was subjected to the standard procedure. Chromatography gave a 3 : 1 mixture of **40** an **40'** as orange colored oil (0.080 g, 55%).

Data of the 3 : 2 mixture of **40**/**40'**: IR (film): 1732*s* (C=O, ester). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): 6.48 br. *s*, H–C(4) of **40'**); 6.40 – 6.32 (superimp. signals of H–C(8,9) of **40'** and H–C(8) of **40**); 6.15 (d-like, H–C(7) of **40**); 6.02 (d-like, 4J(2,Me–C(1)) = 1.4, H–C(2) of **40**); 5.84 (*s*, H–C(10) of **40**); 5.75 (br. *s*, H–C(6) of **40'**); 3.86 and 3.64 (2*s*, MeOOC–C(5) and MeOOC–C(4) of **40'**); 3.67 and 3.61 (2*s*, MeOOC–

C(5) and MeOOC–C(4) of **40**); 2.70 – 2.40 (superimp. signals of Me*C*H_2–C(3), Me_2*C*H–C(9), and Me_2*C*H–C(7) of **40** and **40'**); 2.02 – 1.99 (superimp. signals of Me–C(1,6) of **40** and Me–C(5) of **40'**); 1.66 (*s*, Me–C(10) of **40'**); 1.15 – 1.05 (superimp. signals of *Me*CH_2–C(3), *Me*$_2$CH–C(9), and *Me*$_2$CH–C(7) of **40** and **40'**). EI-MS: 368 (51, M^+), 353 (47, $[M - Me]^+$), 309 (15, $[M - COOMe]^+$), 256 (100, $[M - EtC{\equiv}CCOOMe]^+$).

3.1.6. *Dimethyl (M*,3E,4S*)-3-Ethylidene-9-isopropyl-1,4,6-trimethylheptalene-4,5-dicarboxylate ((M*)-***42***)*. Sulfone (*P**)-**41** (0.100 g, 0.191 mmol) was reacted under the standard conditions with MeONa/MeOH. TLC on silica gel (hexane/Et_2O 4 : 1) gave (*M**)-**42** as orange colored oil (0.015 g, 21%).

*Data of (*M**)-***42**: IR (film): 1732s (C=O, ester). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): 6.55 (br. *s*, H–C(2)); 6.33 (*s*, H–C(10)); 6.26 (*d*, ^3J(8,7) = 6.9, H–C(8)); 6.11 (*dd*-like, ^3J(7,8) = 6.8, ^4J(7,Me–C(6)) = 1.4, H–C(7)); 5.69 (*q*, ^3J(1',Me–C(1')) = 7.0, H–C(1')); 3.74 (*s*, MeOOC–C(5)); 3.49 (*s*, MeOOC–C(4)); 2.51 (*sept*, Me_2C*H*–C(9)); 2.01 (*s*, Me–C(1)); 1.887 (*d*, ^3J(Me–C(1'),1') = 6.8, Me–C(1')); 1.875 (*s*, Me–C(6)); 1.49 (*s*, Me–C(4)); 1.17 and 1.16 (2*d*, J_{vic} = 6.9 and 6.8, *Me*$_2$CH–C(9)). ^{13}C-NMR (150 MHz, $CDCl_3$, 300 K): 176.19 (MeOO*C*–C(4)); 168.79 (MeOO*C*–C(5)); 146.79 (C(9)); 141.74 (C(C5a)); 135.82 (C(3)); 133.31 (C(10a)); 129.97 (C(1)); 129.31 (C(5)); 128.89 (C(6)); 128.31 (C(10)); 127.00 (C(2)); 124.96 (C(1')); 124.61 (C(8)); 124.59 (C(7)); 52.57 (*Me*OOC–C(5)); 51.86 (C(4)); 51.67 (*Me*OOC–C(4)); 26.12 (Me–C(1)); 23.68 and 22.80 (*Me*$_2$CH–C(9)); 22.92 (Me–C(6)); 21.56 (Me–C(4)); 14.02 (Me–C(1')). CI-MS: 400.5 (73, $[M + NH_4]^+$), 385.5 (100, $[M + 1]^+$), 351.4 (25, $[(M + 1) - MeOH]^+$), 279.3 (8, $[(M + 1) - (2\ MeOH + C_3H_4)]^+$).

3.1.7. *Dimethyl 2-Ethyl-9-isopropyl-1,6-dimethylheptalene-4,5-dicarboxylate (***45***)*. The furan-1-one (*P**)-**27** (0.050 g, 0.098 mmol) was reacted for 3 h under the standard conditions. Yield of **45** after chromatography (silica gel, hexane/Et_2O 2 : 1) and crystallization from $CHCl_3$: 0.027 g (81%). No traces of **45'** were found.

Data of **45**: Orange crystals, m.p. 142.2 – 143.1°. R_f (hexane/AcOEt 1 : 1) 0.60. UV/VIS (cyclohexane): max. 323 (sh, 3.13; long tailing up to 400), 283 (3.80), 253 (3.91), 212 (4.06); min. 274 (3.80), 241.5 (3.89). IR (ATR): 1714 (C=O, ester). ^{1}H-NMR (600 MHz, $CDCl_3$, 300 K; C*H*Cl_3 at 7.264): 7.527 (*s*, H–C(2)); 6.254 (*d*, ^3J(8,7) = 6.5, H–C(8)); 6.152 (*d*, ^3J(7,8) = 6.5, H–C(7)); 5.787 (*s*, H–C(10)); 3.705 (*s*, MeOOC–C(5)); 3.697 (*s*, MeOOC–C(4)); 2.476 (*sept*, Me_2C*H*–C(9)); 2.324 (symm. 8 line signal, J_{gem} = 14.8, $J_{vic} \approx$ 7.4, MeCH_2–C(2)); 1.993 (*s*, Me–C(6)); 1.985 (*s*, Me–C(1)); 1.107 (*t*, J_{vic} = 7.6, *Me*CH_2–C(2)); 1.081 and 1.041 (2*d*, J_{vic} = 6.9 and 6.8, *Me*$_2$CH–C(9)). ^{13}C-NMR (150 MHz, $CDCl_3$, 300 K; *C*DCl_3 at 77.23): 167.99 MeOO*C*–C(5)); 167.91 (MeOO*C*–C(4)); 148.78 (C(9)); 144.25 (C(3)); 138.19 (C(2)); 137.10 (C(1)); 133.61 (C(10a)); 130.90 (C(5)); 128.50 (C(6)); 126.88 (C(7)); 125.35 (C(10)); 124.70 (C(8)); 121.99 (C(4)); 52.23 (*Me*OOC–C(4)); 52.13 (*Me*OOC–C(5)); 35.92 (Me_2*C*H–C(9)); 26.71 (Me*C*H_2–C(2)); 23.32 and 22.72 (*Me*$_2$CH–C(9); corr. with 1.107 and 1.080, resp.); 22.41 (Me–C(6)); 21.78 (Me–C(1)); 13.69 (*Me*CH_2–C(2)).

The structural parameters of **45** were determined by an X-ray crytal-structure analysis (*cf*. Table 7).

3.1.8. *Dimethyl 2-Ethyl-6,8,10-trimethylheptalene-4,5-dicarboxylate (***46***) and Dimethyl 4-Ethyl-6,8,10-trimethylheptalene-1,2-dicarboxylate (***46'***)*. Furan-1-one (*P**)-**30** (0.100 g, 0.207 mmol) was reacted and worked up in analogy to 3.1.7. A

thermally equilibrated 3 : 1 mixture of **46** and **46'** was obtained as brownish oil (0.046 g, 65%). R_f (hexane/AcOEt 2 : 1) 0.70.

Data of **46**: ^{1}H-NMR (600 MHz, $CDCl_3$, 300 K, 74% of **46**; C*H*Cl_3 at 7.260): 7.50 (*s*, H–C(3)); 6.13 (br. *s*, H–C(9)); 5.94 (br. *s*, H–C(7)); 5.79 (br. *s*, H–C(1)); 3.72 (s, MeOOC–C(4)); 3.69 (s, MeOOC–C(5)); 2.33 (symm. *m*, J_{gem} = 15.0, J_{vic} = 7.5, ^4J(MeC*H*$_2$–C(2),1) = 1.3, MeC*H*$_2$–C(2)); 2.01 (br. *s*, Me–C(8)); 1.97 (*d*, ^4J(Me–C(6),7) = 1.1, Me–C(6)); 1.73 (*s*, Me–C(10)); 1.16 (*t*, J_{vic} = 7.5, *Me*CH$_2$–C(2)). ^{13}C-NMR (150 MHz, $CDCl_3$, 300 K, 74% of **46**; *C*DCl_3 at 77.00): 167.96 (MeOO*C*–C(4)); 167.53 (MeOO*C*–C(5)); 148.43 (C(5a)); 143.70 (C(2)); 142.55 (C(3)); 139.46 (C(8)); 132.98 (C(4)); 132.05 (C(10)); 130.24 (C(9)); 129.90 (C(6)); 129.80 (C(1)); 129.20 (C(7)); 122.87 (C(5)); 122.54 (C(10a)); 52.12 (*Me*OOC–C(4)); 51.87 (*Me*OOC–C(5)); 29.06 (Me*C*H$_2$–C(2)); 24.91 (Me–C(8)); 23.31 (Me–C(6)); 17.84 (Me–C(10)); 14.01 (*Me*CH$_2$–C(2)).

Data of **46'**: ^{1}H-NMR (600 MHz, $CDCl_3$, 300 K, 24% of **46'**; C*H*Cl_3 at 7.260): 6.26 (*q*-like, ^4J(3,MeC*H*$_2$–C(4)) ≈ ^4J(3,5) = 1.1, H–C(3)); 6.09 (br. *s*, H–C(9)); 5.91 (*quint*-like, H–C(7)); 5.72 (*d*, ^4J(5,3) = 1.1, H–C(5)); 3.83 (*s*, MeOOC–C(2)); 3.70 (*s*, MeOOC–C(1)); 2.30 (symm. *m*, J_{gem} = 14.0, J_{vic} = 7.4, ^4J(MeC*H*$_2$–C(4),3) ≈ 0.7, MeC*H*$_2$–C(4)); 2.11 (*d*, ^4J(Me–C(6)),7) = 1.1, Me–C(6)); 1.96 (*d*, ^4J(Me–C(8),9) = 1.1, Me–C(8)); 1.63 (*s*, Me–C(10)); 1.08 (*t*, J_{vic} = 7.5, *Me*CH$_2$–C4)). ^{13}C-NMR (150 MHz, $CDCl_3$, 300 K, 24% of **46'**; *C*DCl_3 at 77.00; assigned signals): 168.82 (MeOO*C*–C(4)); 166.97 (MeOO*C*–C(5)); 151.53 (C(4)); 144.18 (C(5a)); 141.46 (C(10)); 139.19 (C(8)); 134.79 (C(6)); 134.11 (C(1)); 131.29 (C(9)); 130.03 (C(7)); 125.30 (C(5)); 124.58 (C(2)); 122.53 (C(10a)); 122.25 (C(3)).

3.1.9. *Dimethyl 2-Ethyl-1,6,8,10-tetramethylheptalene-4,5-dicarboxylate (***47***) and Dimethyl 4-Ethyl-5,6,8,10-tetramethylheptalene-1,2-dicarboxylate (***47'***)*. Furan-1-one (*P**)-**31** (0.091 g, 0.203 mmol) was reacted in analogy to 3.1.7. All starting material had been consumed after 0.75 h. Chromatography (silica gel, hexane/AcOEt 3 : 1) gave in a first fraction a 1 : 9 mixture of **47** and **47'** as brownish oil (0.048 g, 67 %). In a second fraction, we found small amounts (*ca*. 5 mg, 5 %) of the corresponding anhydride of (P*)-31, (P*,5R*)-6,7,9,11-tetramethyl-5-((S*)-1-(phenylsulfonyl)-ethyl)-4,5-dihydro- heptaleno[1,2-*c*]furan-1,3-dione ((*P**)-**48**). On standing in $CDCl_3$ solution over two month at ambient temperature in the laboratory, the 1 : 9 mixture of **47** and **47'** was nearly completely converted into **47** (residual amount of **47'** max. 8 %).

Data of **47** *after isomerization*: ^{1}H-NMR (600 MHz, $CDCl_3$; *C*DCl_3 at 7.260): 7.56 (*d*-like, ^5J(3,Me–C(1)) ≈ 0.7, H–C(3)); 6.14 (br. *s*, H–C(9)); 6.01 (br. *s*, H–C(7)); 3.70 (*s*, MeOOC–C(4)); 3.69 (*s*, MeOOC–C(5)); 2.34 (symm. 10 line *m*, J_{gem} = 12.0, J_{vic} = 7.6, Me*C*H_2–C(2)); 2.04 (*d*, ^4J(Me–C(8),9) = 1.2, Me–C(8)); 1.96 (*d*, ^4J(Me–C(6),7) = 1.2, Me–C(6)); 1.90 (*d*-like, ^5J(Me–C(1),Me*C*H_2–C(2)) ≈ ^5J(Me–C(1),3) ≈ 0.7, Me–C(1)); 1.70 (*s*, Me–C(10)); 1.11 (*t*, J_{vic} = 7.6, *Me*CH_2–C(2)). ^{13}C-NMR (150 MHz, $CDCl_3$; *C*DCl_3 at 77.00): 167.85 (MeOO*C*–C(4)); 167.75 (MeOO*C*–C(5)); 146.89 (C(5a)); 143.36 (C(3)); 138.49 (C(2)); 138.47 (C(8)); 136.07 (C(1)); 130.31 (C(9)); 130.23 (C(6)); 130.15 (C(4)); 129.45 (C(10)); 128.59 (C(7)); 127.49 (C(10a)); 121.36 (C(5)); 52.01 (*Me*OOC–C(4)); 51.79 (*Me*OOC–C(5)); 25.86 (Me*C*H_2–C(2)); 25.04 (Me–C(6)); 19.81 (Me–C(1)); 18.20 (Me–C(10)); 13.68 (*Me*CH_2–C(2)).

Data of **47'**: ^{1}H-NMR (300 MHz, $CDCl_3$; in the presence of *ca*. 10 % of **47**; C*H*Cl_3 at 7.260): 6.44 (*s*, H–C(3)); 6.05 (br. *s*, H–C(9)); 5.96 (br. *s*, H–C(7)); 3.82 (*s*, MeOOC–

C(2)); 3.70 (s, MeOOC–C(1)); 2.42 (*ddd*, J_{gem} = 15.0, J_{vic} = 7.5, ^4J(MeCH_AH$_B$–C(2),3) = 1.3, MeCH_AH$_B$–C(2)); 2.28 (*ddd*, J_{gem} = 15.0, J_{vic} = 7.4, ^4J(MeCH$_A$$H_B$–C(2),3) = 0.8, MeCH$_A$$H_B$–C(2)); 2.04 (*d*, ^4J(Me–C(6),7) = 1.2, Me–C(6)); 1.99 (*d*, ^4J(Me–C(8),9) = 1.1, Me–C(8)); 1.75 (*s*, Me–C(10)); 1.00 (*t*, J_{vic} = 7.4, *Me*CH$_2$–C(4)). ^{13}C-NMR (75 MHz, CDCl$_3$; *C*DCl$_3$ at 77.00; assigned signals): 129.96 (C(9)); 128.85 (C(7)); 122.76 (C(3)); 52.40 (*Me*OOC–C(4)); 52.21 (MeOO*C*–C(5)); 30.15 (Me*C*H$_2$–C(4)); 24.97 (Me–C(8)); 22.54 (Me–C(5)); 17.60 (Me–C(10)); 14.55 (Me–C(6)); 13.82 (*Me*CH$_2$–C(4)).

*Data of (*P**)*-**48**: ^{1}H-NMR (300 MHz, CDCl$_3$; CHCl$_3$ at 7.260): 7.73 (H$_o$ of PhSO$_2$); 7.64 (H$_p$ of PhSO$_2$); 7.52 (H$_m$ of PhSO$_2$); 6.20 (*s*, H–C(10)); 6.00 (*s*, H–C(8)); 3.65 (*sext*-like, ^3J(1',Me–C(1')) = 7.2, ^3J(1',5) = 9.5, H–C(1')); 3.01 (*dt*, ^3J(5,1') = 9.5, ^3J(1',H$_S$) = 3.4, ^3J(1',H$_R$) = 4.4, H–C(5)); 2.86 (*dd*, ^2J(H$_S$,H$_R$) =14.7, ^3J(H$_S$,5) = 3.4, H$_S$–C(4)); 2.79 (*dd*, ^2J(H$_R$,H$_S$) = 14.7, ^3J(H$_R$,5) = 4.4, H$_R$–C(4)); 2.11 (*s*, Me–C(9)); 1.94 (*s*, Me–C(7)), 1.92 (*s*, Me–C(11)); 1.75 (*s*, Me–C(6)); 1.15 (*d*, ^3J(Me–C(1'),1') = 7.2, Me–C(1')).

4. Crystal-Structure Determination of 4, **5**, **10**, **27**, **30**, **31**, **41**, **45, and 48** (*Table 7* and *Figs. 2 – 6*)[20]. – All measurements were conducted using graphite-monochromated MoK_α radiation (λ = 0.71073 Å). For **27**, **30**, **31**, **41**, and **45**, a *Nonius KappaCCD* area detector diffractometer [18,19] and an *Oxford Cryosystems Cryostream 700* cooler were employed, while data for the remaining compounds were

[20]) CCDC-761780–761788 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data request/cif.

collected on a *Rigaku AFC5R* diffractometer [20] mounted on a 12kW rotating anode generator. The data collection and refinement parameters are given in *Table 7*, views of the molecules are shown in *Figs. 2 – 6*. The intensities were corrected for *Lorentz* and polarization effects, and an absorption correction based on the multi-scan method [21] was applied for **30** and **31**. Each structure was solved by direct methods using either *SIR92* [22] or *SHELXS97* [23], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent atom ($1.5U_{eq}$ for the methyl groups). The refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimised the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was applied in the cases of **5**, **27**, **30**, **31**, **41**, and **45**. For **41** and **45**, six and four reflections, respectively, whose intensities were considered to be extreme outliers, were omitted from the final refinement.

Compound **4** crystallises in a non-centrosymmetric polar space group and refinement of the absolute structure parameter yielded a value of 0.47(9), which indicates that the crystals are inversion twins and that the compound is racemic. Compound **48** also crystallises in a non-centrosymmetric polar space group, but the absolute structure has not been determined and has been assigned arbitrarily. The structure of **27** has two symmetry-independent molecules in the asymmetric unit. In the structure of **45**, one terminal Me group of the iPr group is disordered. Two positions were defined for this group and refinement of constrained site occupation factors yielded a value of 0.850(6) for the major conformation. Similarity restraints were applied to the bond

lengths involving the disordered C-atoms and they were restrained to have similar atomic displacement parameters.

Neutral atom scattering factors for non-hydrogen atoms were taken from [24a], and the scattering factors for H-atoms were taken from [25]. Anomalous dispersion effects were included in F_c [26]; the values for f' and f'' were those of [24b]. The values of the mass attenuation coefficients are those of [24c]. All calculations were performed using the *SHELXL97* program [23]. The crystallographic diagrams were drawn using *ORTEPII* [27].

Table 7. *Crystallographic Data for Compounds* **4**, **5**, **10**, **27**, **30**, **31**, **41**, **45**, *and* **48**

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Text to Figures

Fig. 1. *Stereoscopic view of the AM1 calculated structure of (*P*,5*S*)-8-isopropyl-3,3-dimethoxy-6,11-dimethyl-5-((*R*)-1-(phenylsulfonyl)ethyl)-4,5-dihydroheptaleno[1,2-*c*]furan-1-one* (**27**) *with dotted* van der Waals *surfaces of O=C(1) and Me–C(11)*

Fig. 2. *Stereoscopic view of the X-ray crystal structure of dimethyl (*P**,3*R**,4*R**)-1-methyl-3-(phenylsulfonylmethyl)-3,4-dihydroheptalene-4,5-dicarboxylate* (**4**) (50% probability ellipsoids)

Fig. 3. *Stereoscopic view of the X-ray crystal structure of dimethyl (*P**,3*S**,4*S**)-1,6-dimethyl-3-((phenylsulfonyl)methyl)-3,4-dihydro-heptalene-4,5-dicarboxylate* (**10**) (50% probability ellipsoids)

Fig. 4. *Stereoscopic view of the X-ray crystal structure of dimethyl (*P**, 3*S**,4*S**)-9-isopropyl-1,4,6-trimethyl-3-((*S**)-1-(phenylsulfonyl)ethyl)-3,4-dihydroheptalene-4,5-dicarboxylate* (**41**) (50% probability ellipsoids)

Fig. 5. *Stereoscopic view of the X-ray crystal structure of one of the two symmetry-independent molecules (*P**,5*S**)-8-isopropyl-3,3-dimethoxy-5-((*R**)-1-(phenylsulfonyl)ethyl)-4,5-dihydroheptaleno[1,2-*c*]furan-1-one* (**27**) (50% probability ellipsoids)

Fig. 6. *Stereoscopic view of the X-ray crystal structure of (*P**,5*R**)-3,3-dimethoxy-6,7,9,11-tetramethyl-5-((*S**)-1-(phenylsulfonyl)ethyl)-4,5-dihydroheptaleno[1,2-*c*]furan-1-one* (**31**) (50% probability ellipsoids)

Fig. 7. *AM1 calculated, hypothetical dienolate structures resulting from* re *and* si *attack* (a) and b), respectively) *of methanide at C(5) of (*P*)-configured 1-furanone* **28** (see text)

KAH, ZAM, AL; HJH

Fig. 1

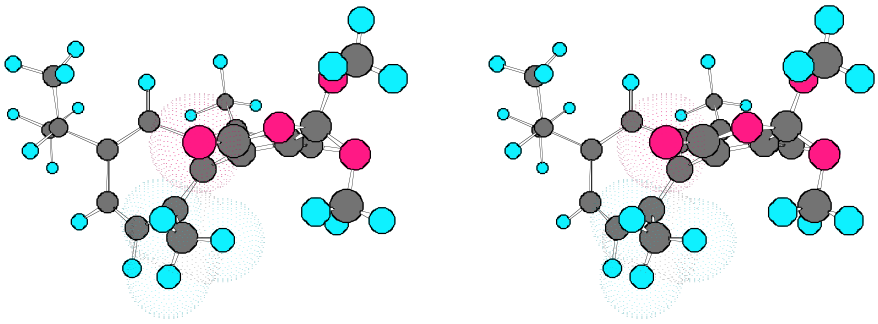


Fig. 2

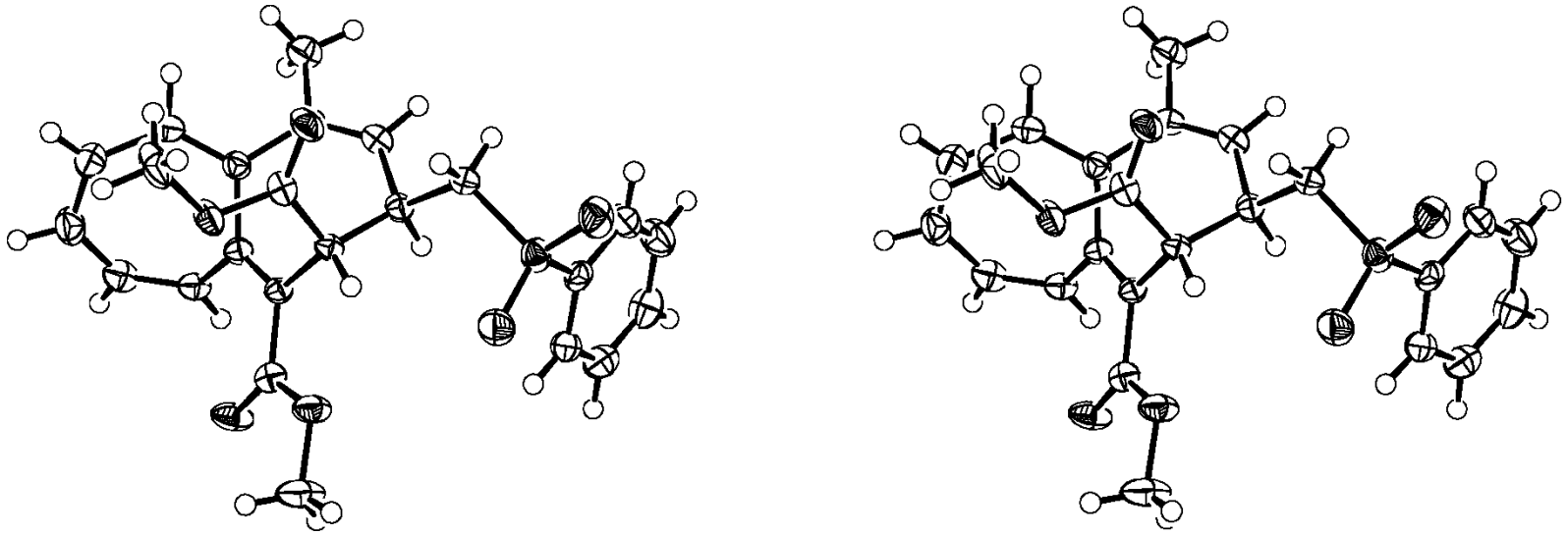
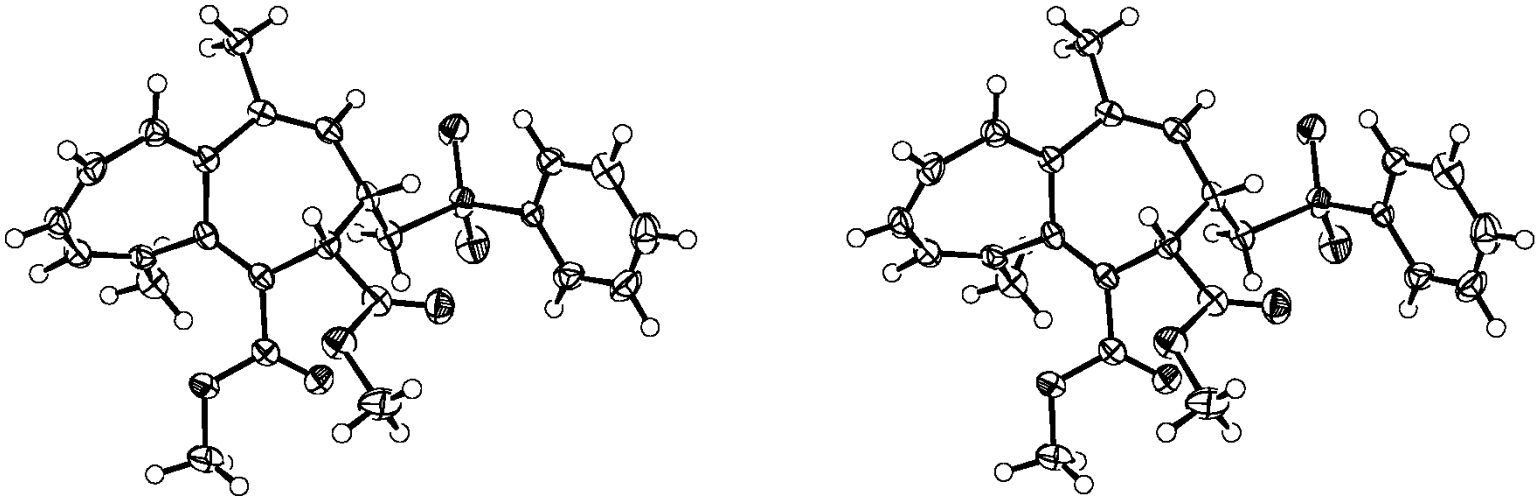
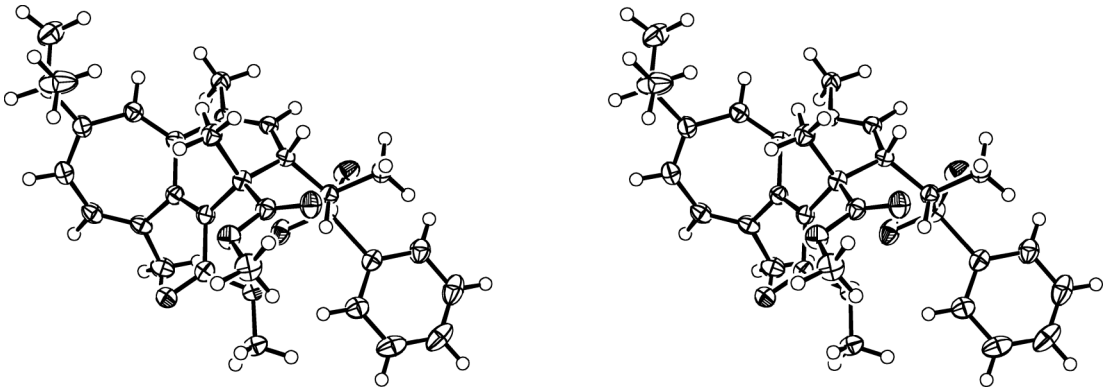


Fig. 3



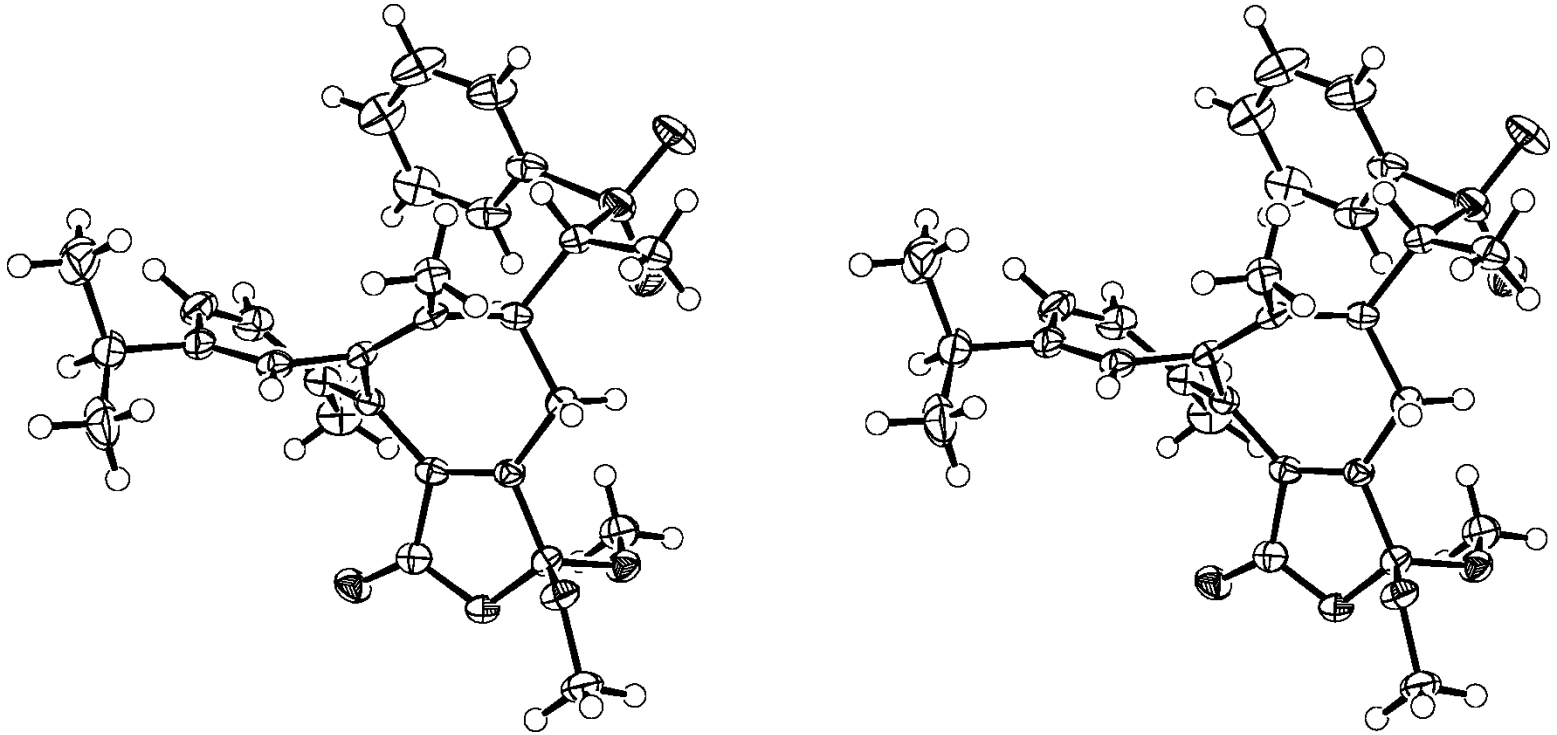
KAH,ZAM,AL,HJH

Fig. 4



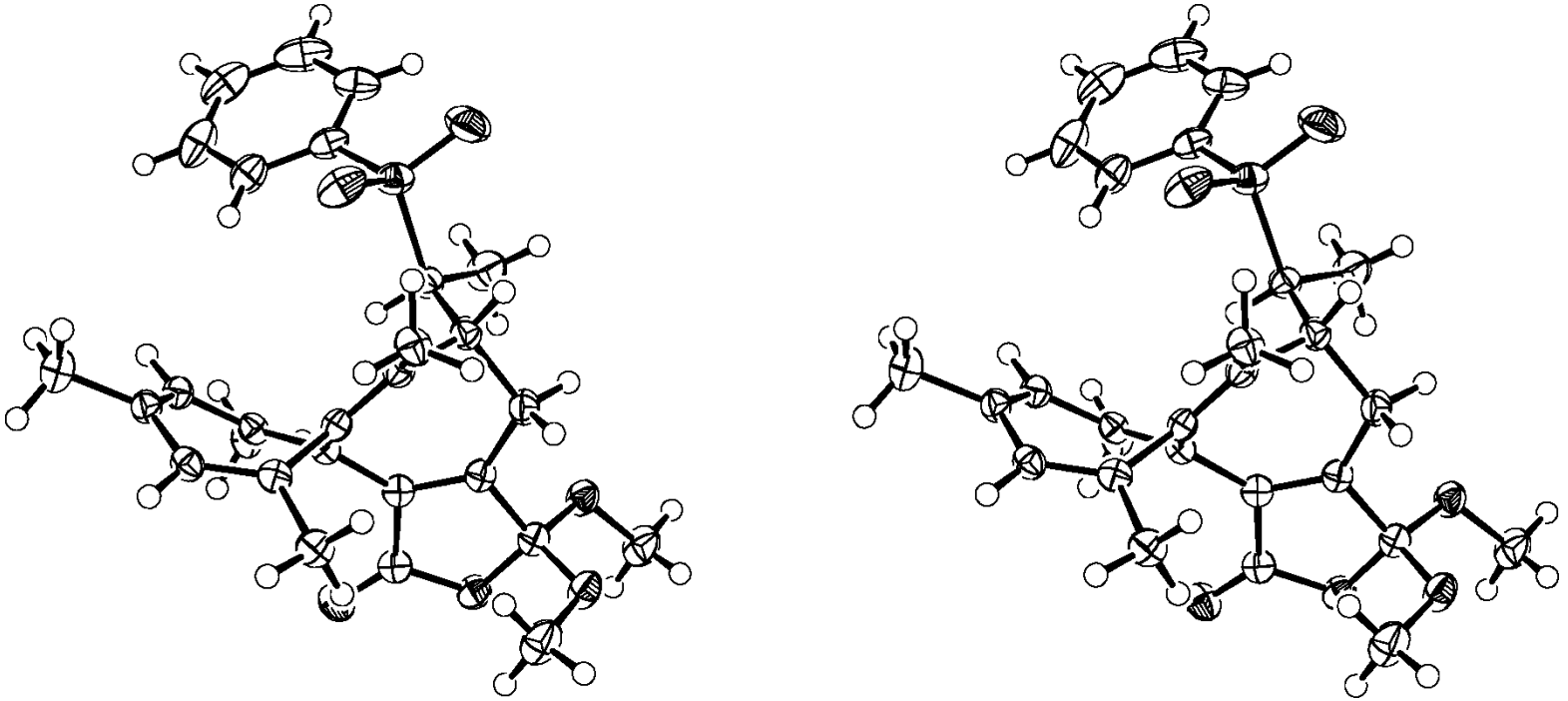
KAH,ZAM,AL,HJH

Fig. 5



KAH,ZAM,AL,HJH

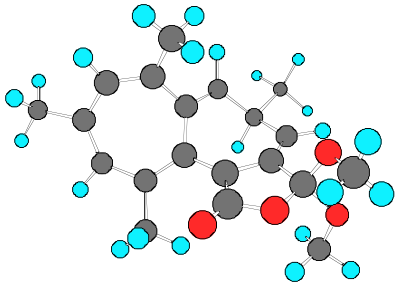
Fig. 6



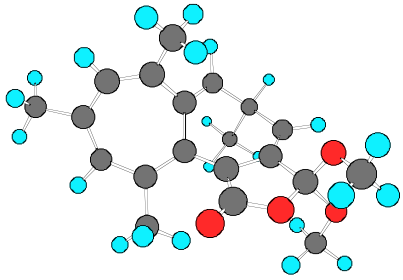
KAH, ZAM, AL, HJH

Fig. 7

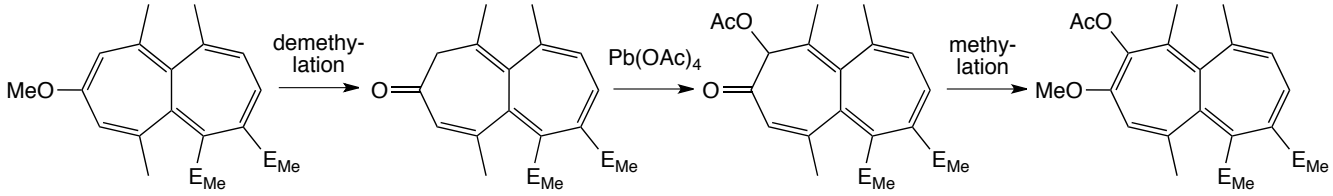
a)



b)



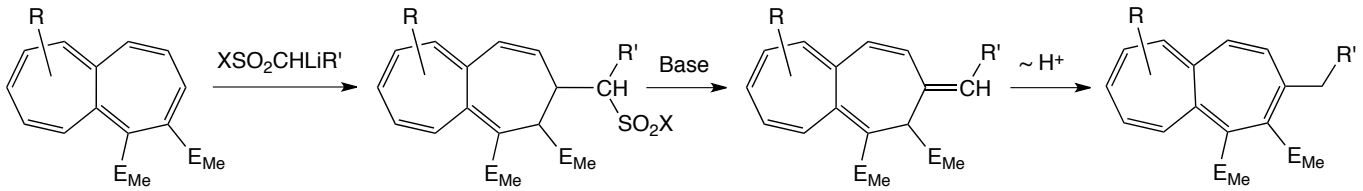
Scheme 1[a])



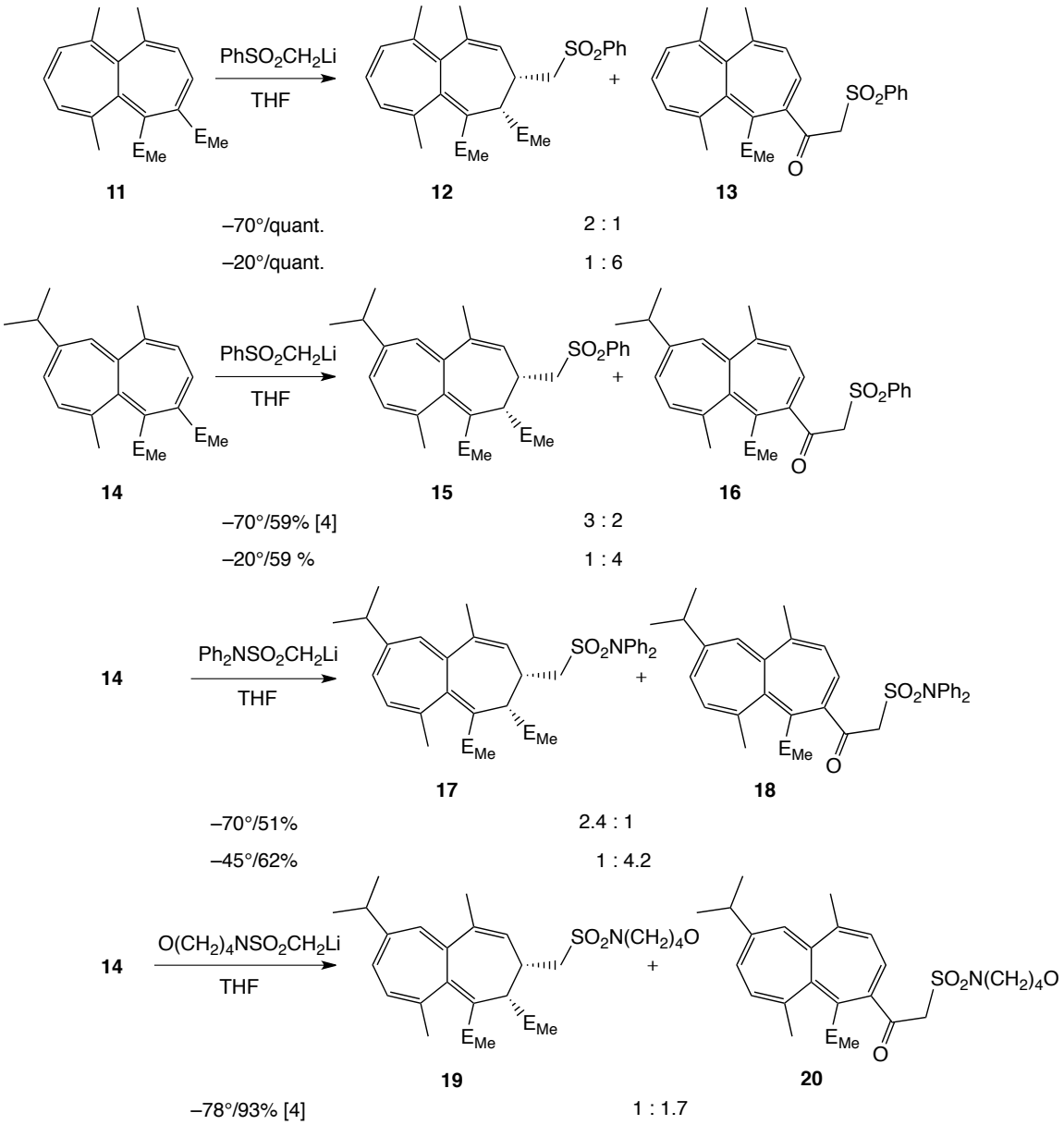
[a]) E_{Me} = COOMe in all schemes.

KAH,ZAM,PG,RWK,AL,HJH

Scheme 2

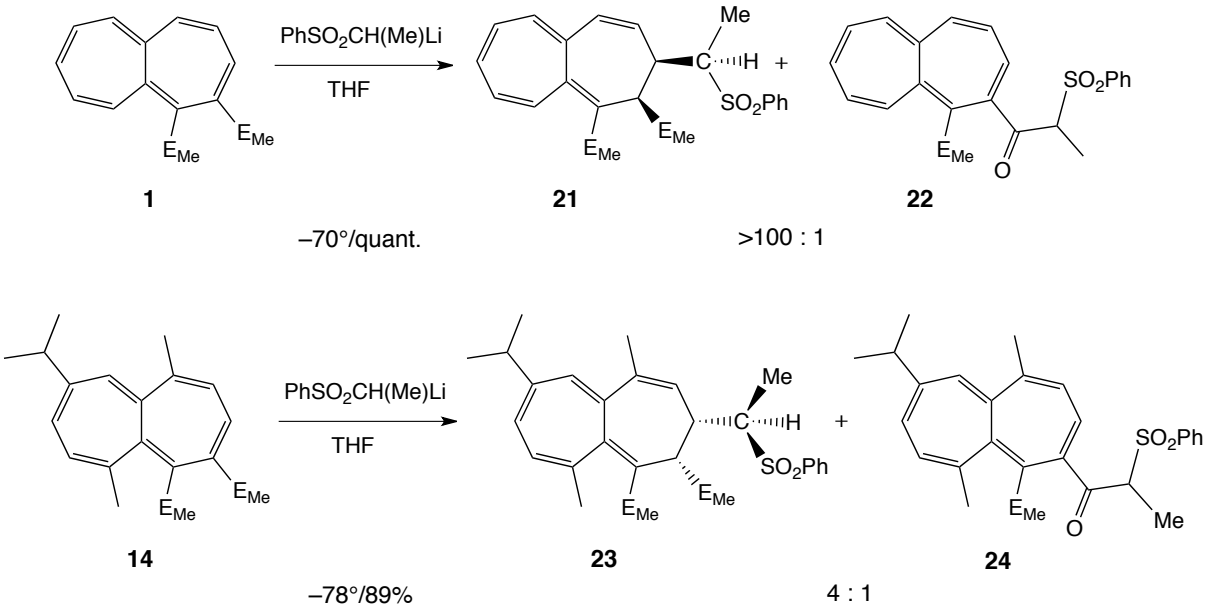


Scheme 3

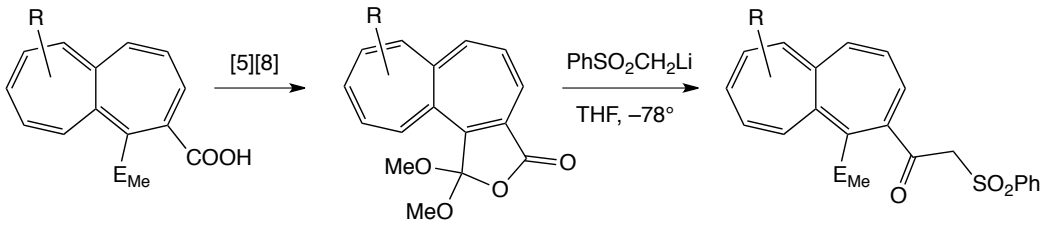

PhSO2CH2Li
THF
SO2Ph
EMe
11
12
13
–70°/quant.
2 : 1
–20°/quant.
1 : 6
14
15
16
–70°/59% [4]
3 : 2
–20°/59 %
1 : 4
Ph2NSO2CH2Li
SO2NPh2
17
18
–70°/51%
2.4 : 1
–45°/62%
1 : 4.2
O(CH2)4NSO2CH2Li
SO2N(CH2)4O
19
20
–78°/93% [4]
1 : 1.7

KAH,ZAM,PG,RWK,AL,HJH

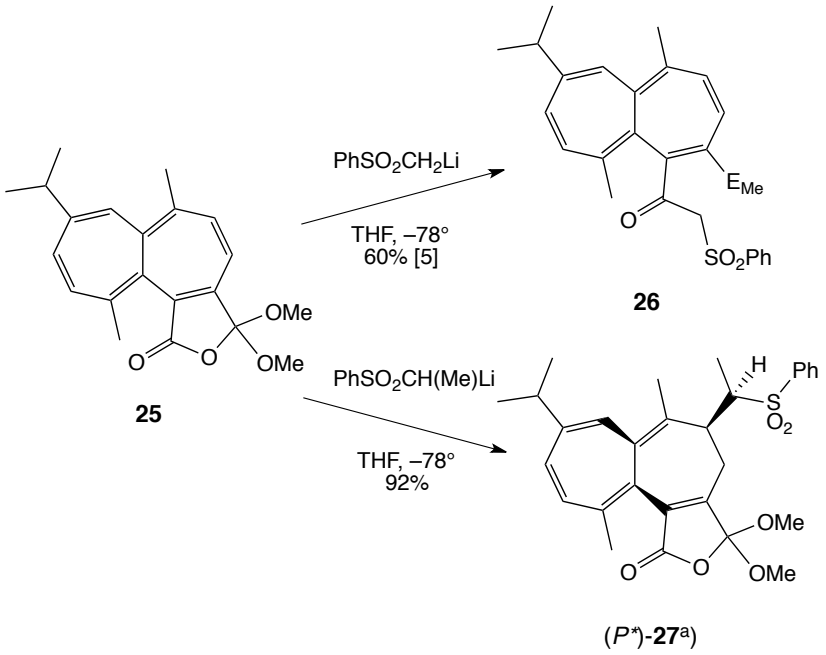
Scheme 4



Scheme 5

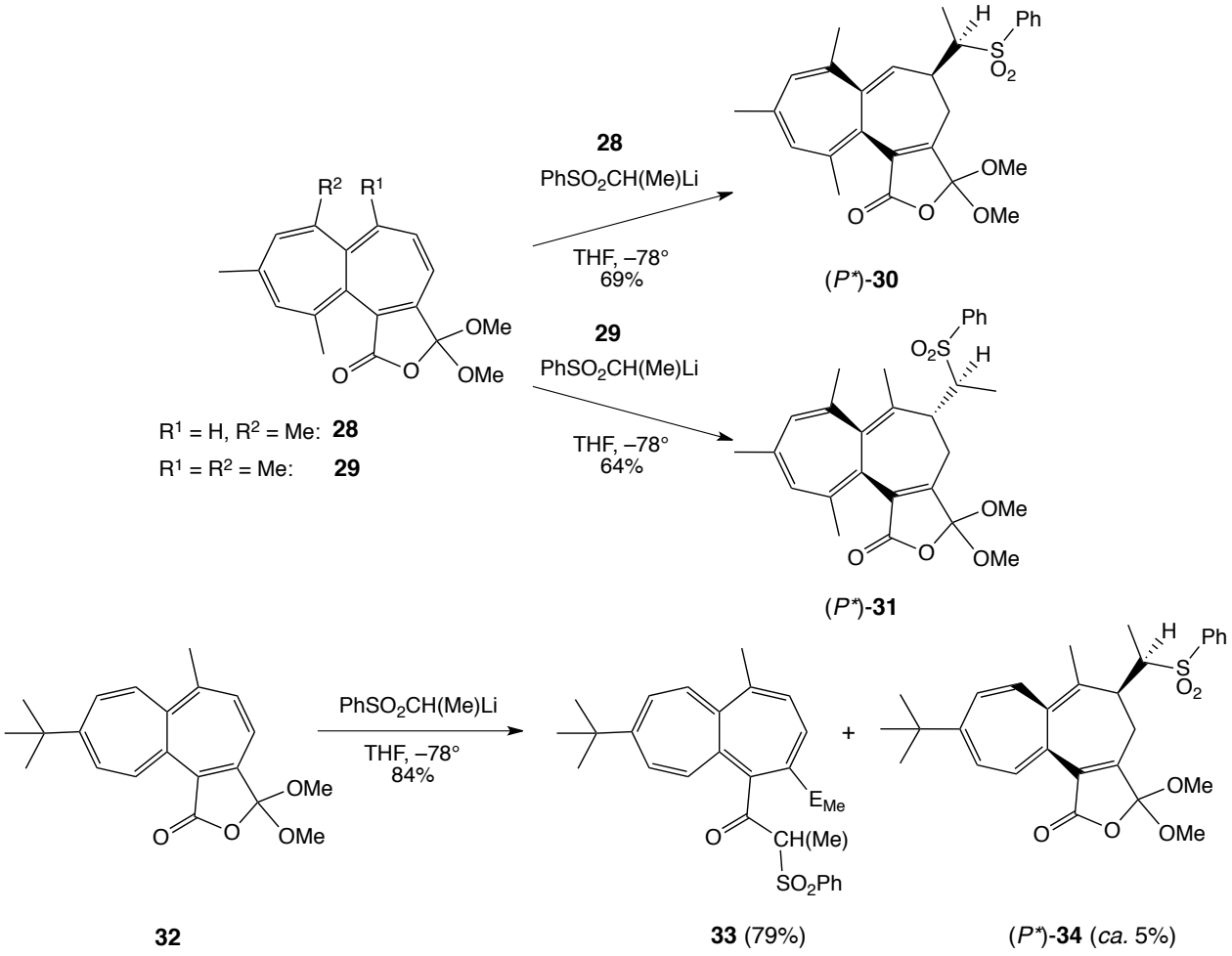

R
[5][8]
COOH
E_{Me}
MeO
MeO
O
O
$PhSO_2CH_2Li$
THF, –78°
SO_2Ph
furan-3-one type
OMe
OMe
furan-1-one type
PhO_2S

Scheme 6

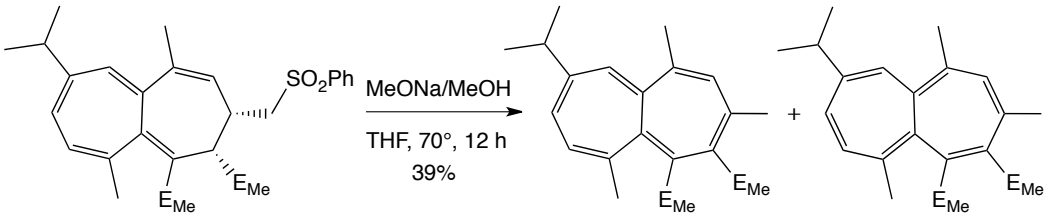


a) The (*P**)-configuration of **27** in the crystals is shown. In solution at ambient temperature, a 64 : 36 mixture of (*P**)- and (*M**)-**27** is established in a short time.

Scheme 7


28
PhSO2CH(Me)Li
THF, –78°
69%
(P*)-30
29
PhSO2CH(Me)Li
THF, –78°
64%
(P*)-31
R1 = H, R2 = Me: 28
R1 = R2 = Me: 29
PhSO2CH(Me)Li
THF, –78°
84%
32
33 (79%)
(P*)-34 (ca. 5%)

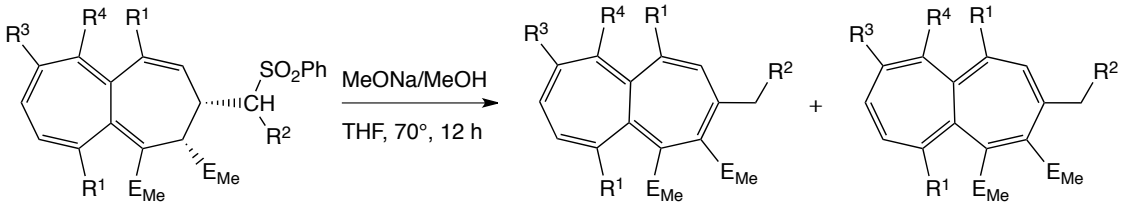
Scheme 8



15 **35** 3 : 2 **35'**

KAH,ZAM,PG,RWK,AL,HJH

Scheme 9



$R^1 – R^4$ = H :	**2**	30%[a])	**36**[b])		**36'**
R^1 = Me, $R^2 – R^4$ = H :	**10**	66%	**38**[c])	2 : 1	**38'**
R^1, R^4 = Me, R^2, R^3 = H :	**12**	27%	**39** (18%)[d])		**39'** (9%)
R^1, R^2 = Me, R^3 = iPr, R^4 = H :	**23**	55%	**40**[b])	3 : 1	**40'**

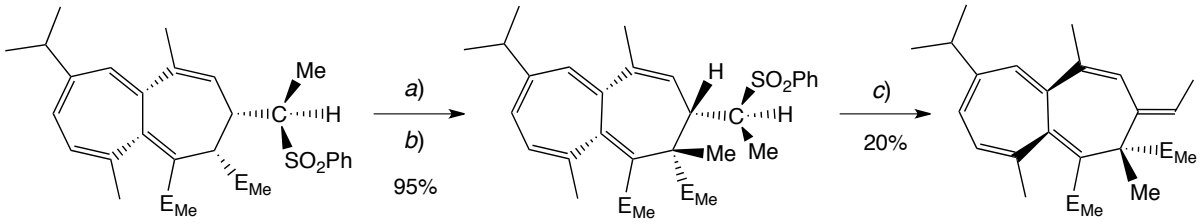
[a]) *t*-BuOK/THF was used instead of MeONa/MeOH; for the latter base see later.

[b]) Mainly the 4,5-diester form was recognizable in the NMR spectra.

[c]) Slow interconversion of both DBS forms at r.t.

[d]) Yield after chromatographic separation and crystallization of both DBS isomers.

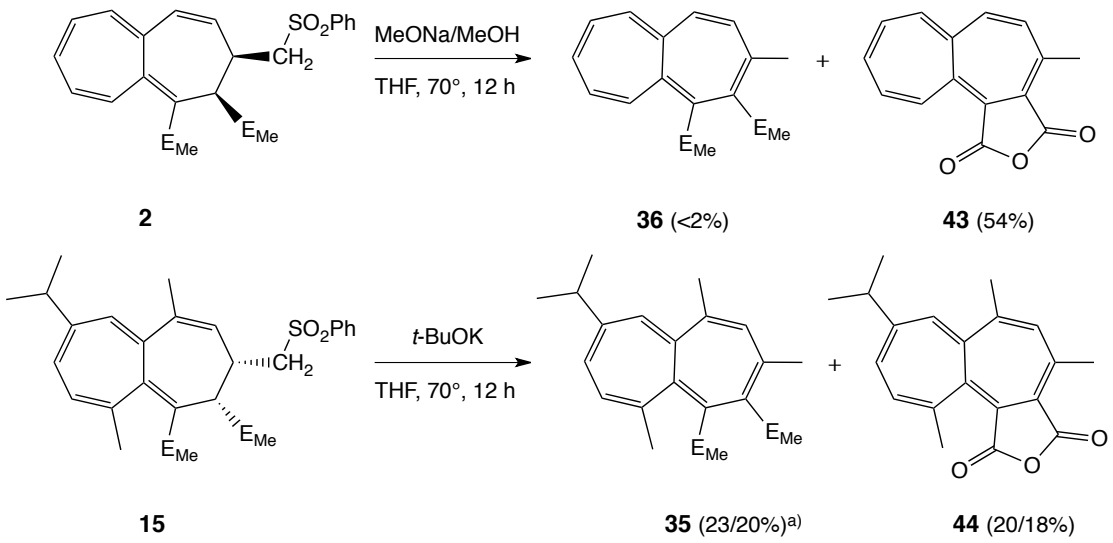
Scheme 10



(*P**)-**23** (*P**)-**41** (*M**)-**42**

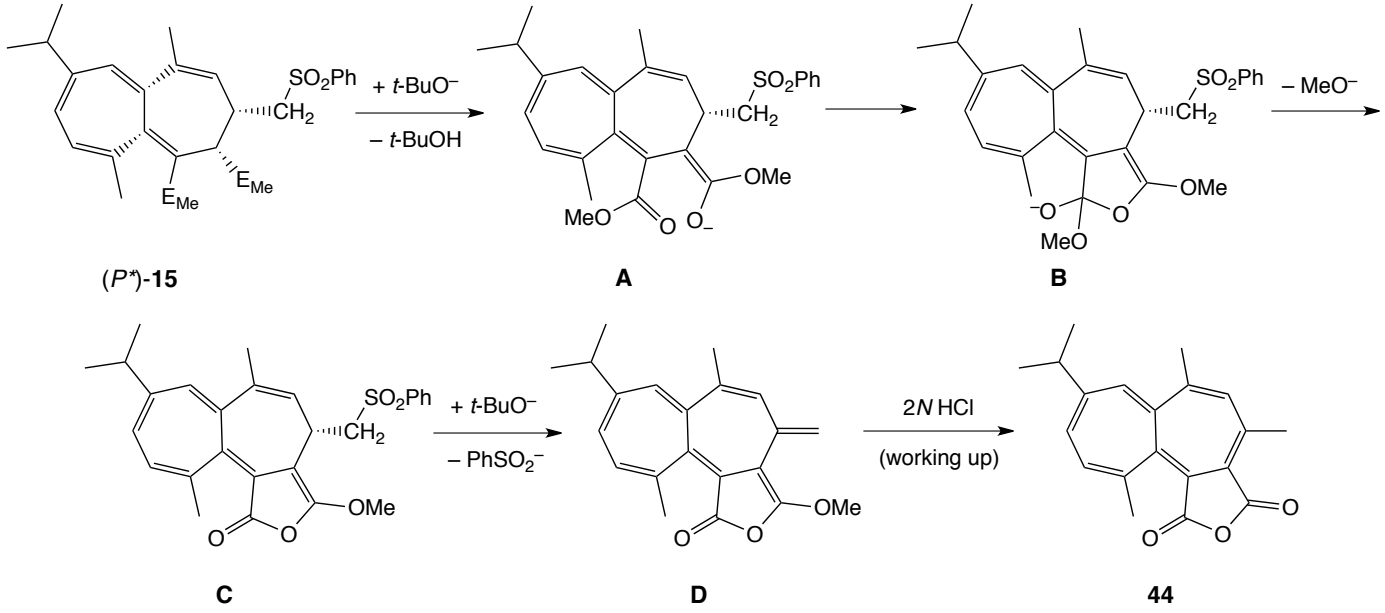
a) NaH/THF, 4 h, – 10° to r.t. *b*) MeI, 3 d, r.t. *c*) MeONa/MeOH, THF, 70°, 12 h.

Scheme 11

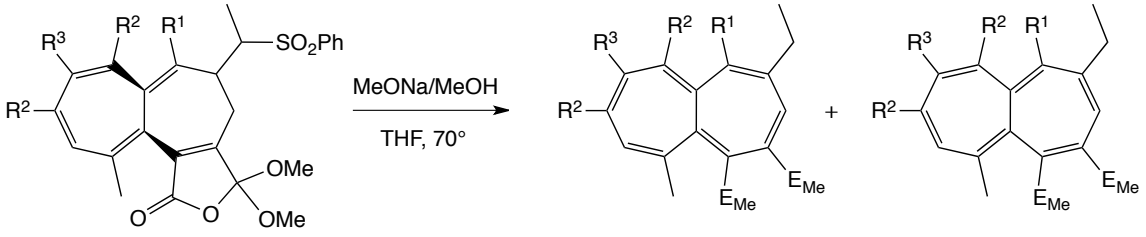


a) 3 : 1 Mixture of the DBS isomers. Second yield corresponds to Et_3COK as base.

Scheme 12


SO2Ph
CH2
+ t-BuO–
– t-BuOH
EMe
EMe
MeO
O
O–
OMe
– MeO–
–O
O
MeO
(P*)-15
A
B
+ t-BuO–
– PhSO2–
2N HCl
(working up)
C
D
44

Scheme 13



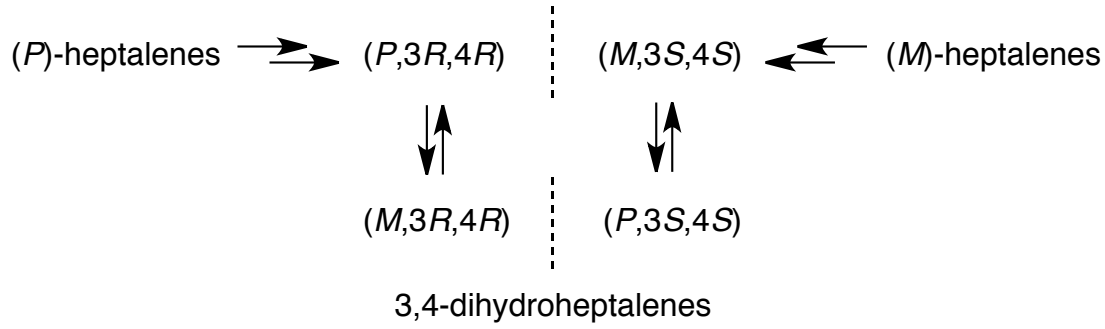
R^1 = Me, R^2 = H, R^3 = iPr :	**27**	3 h/81%	**45**	>200 : 1[a])	**45'**
R^1, R^3 = H, R^2 = Me :	**30**	3 h/65%	**46**	3 : 1[a])	**46'**
R^1, R^2 = Me, R^3 = H :	**31**	0.75 h/67%[b])	**47**	1 : 9[c])	**47'**

[a]) Represents the thermal equilibrium mixture.

[b]) The anhydride **48** (*ca.* 5%) of **31** was found in addition.

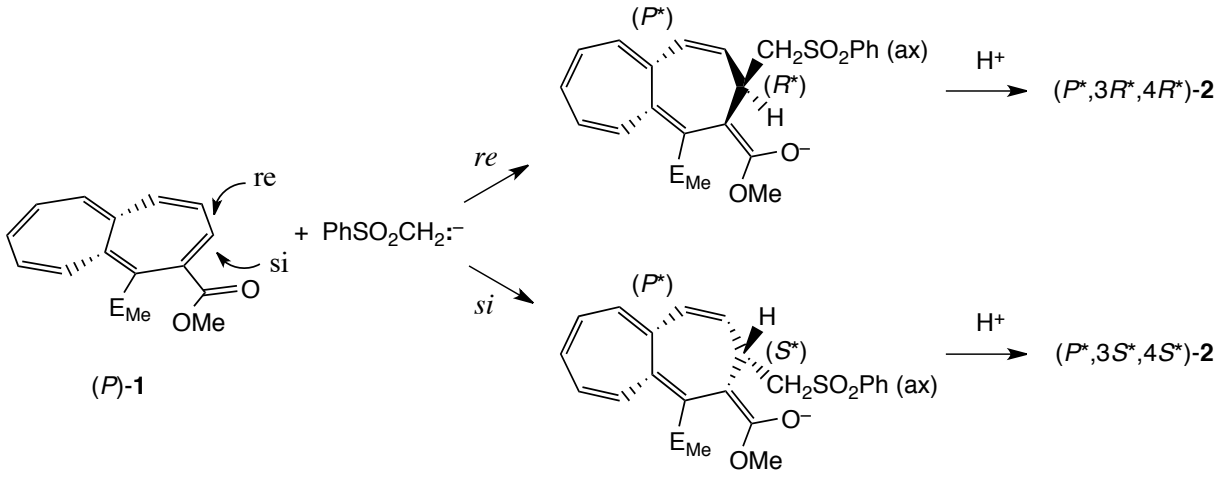
[c]) The ratio of the thermal equilibrium mixture for the corresponding 2-/4-methyl analogs at 180° amounts to 3.3 : 1 (*cf.* [10]).

Scheme 14

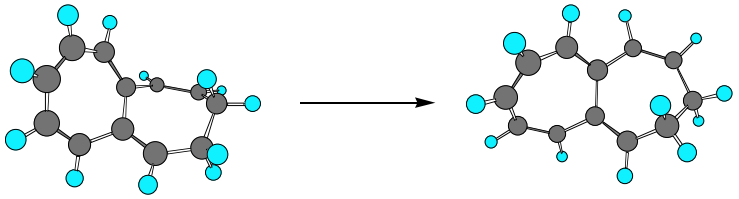

(*P*)-heptalenes
(*P*,3*R*,4*R*)
(*M*,3*S*,4*S*)
(*M*)-heptalenes
(*M*,3*R*,4*R*)
(*P*,3*S*,4*S*)
3,4-dihydroheptalenes

KAH,ZAM,PG,RWK,AL,HJH

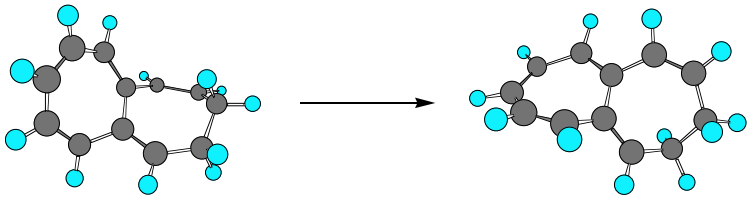
Scheme 15



Scheme 16



	(–)-sc-(*P*)	TS	(+)-sc-(*P*)
ΔH_f°[a])	68.59	71.57	67.19
Θ [°][b])	–59.5	0	66.2



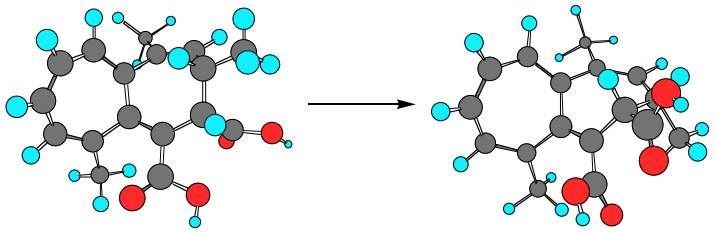
	(–)-sc-(*P*)	TS	(–)-sc-(*M*)
ΔH_f°[a])	68.59	75.19	67.19
Θ [°][c])	224.2	178	129.0

[a]) Kcal·mol^{-1}.

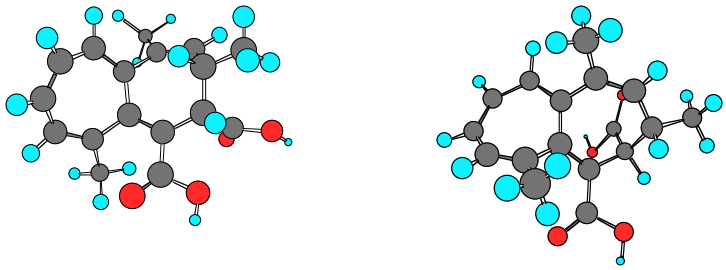
[b]) Θ (C(2)–C(3)–C(4}–C(5)).

[c]) Θ (C(5)=C(5a)–C(10a)=C(10)).

Scheme 17



	(–)-sc-(*P*,3*S*,4*S*)	TS	(+)-sc-(*P*,3*S*,4*S*)
ΔH_f°[a])	–116.74	–114.34	–118.44
Θ [°][b])	–69.5	0	65.0



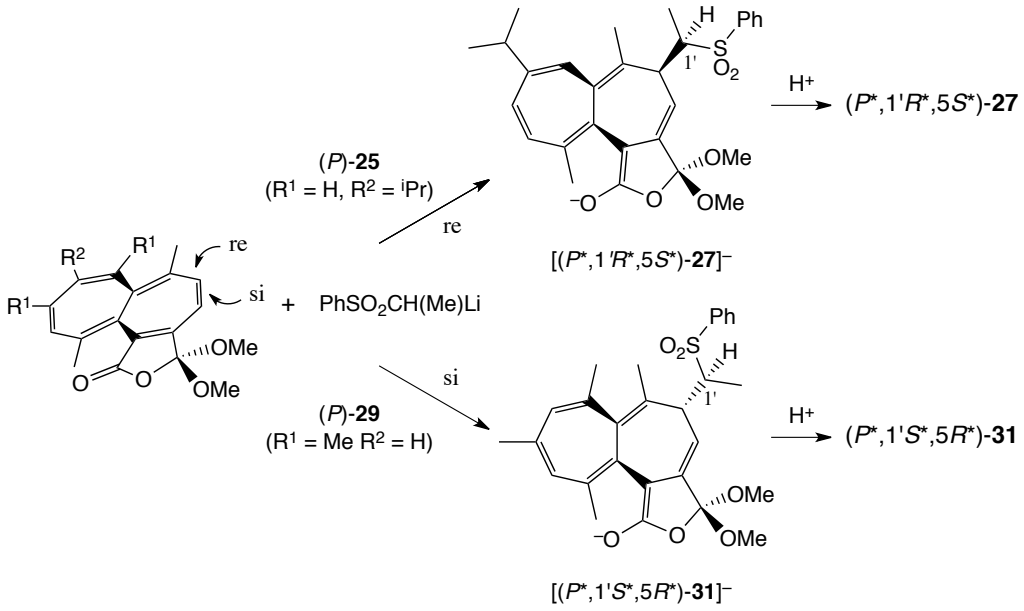
	(–)-sc-(*P*,3*S*,4*S*)	TS	(–)-sc-(*M*,3*S*,4*S*)
ΔH_f°[a])	–116.74	–99.85	–117.30
Θ [°][c])	234.7	180	119.8

[a]) Kcal·mol^{-1}.

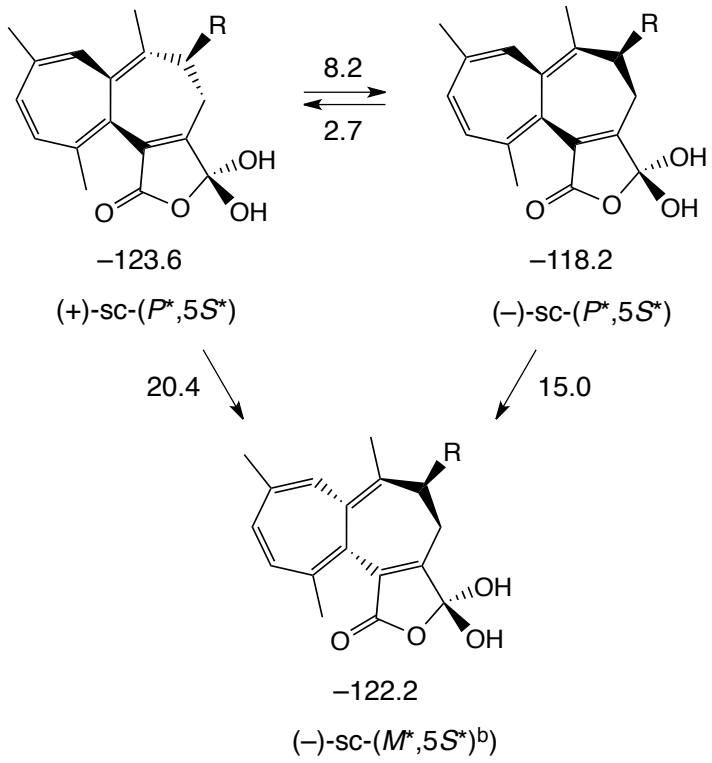
[b]) Θ (C(2)–C(3)–C(4)–C(5)).

[c]) Θ (C(5)=C(5a)–C(10a)=C(10)).

Scheme 18


(P)-25
(R1 = H, R2 = iPr)
re
si
+ PhSO2CH(Me)Li
(P)-29
(R1 = Me R2 = H)
re
si
H
Ph
S
O2
1'
OMe
OMe
O
O
H+
(P*,1'R*,5S*)-27
[(P*,1'R*,5S*)-27]–
Ph
O2S
H
1'
OMe
OMe
O
O
H+
(P*,1'S*,5R*)-31
[(P*,1'S*,5R*)-31]–

Scheme19[a])

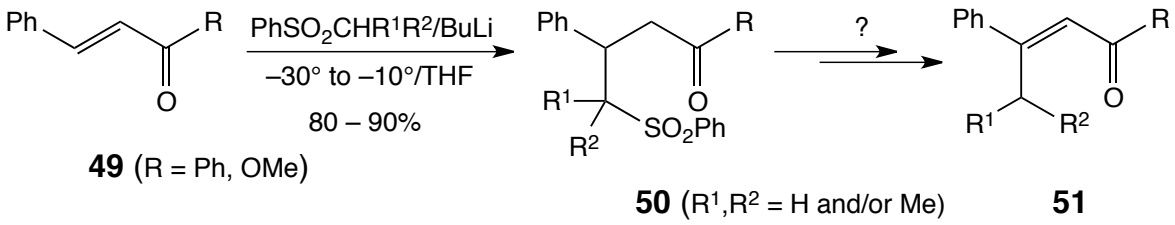


[a]) AM1 calculated $\Delta H_f°$ and $\Delta H_f^{\ddagger}$ in Kcal·mol^{-1} for R = Me.

[b]) (+)-sc-(*M**,5*S**): –118.4.

KAH,ZAM,PG,RWK,AL,HJH

Scheme 20

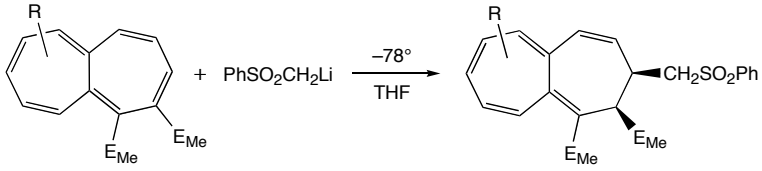


49 (R = Ph, OMe)

50 (R^1,R^2 = H and/or Me)

51

Table 1. Michael *Addition Reaction of ((Phenylsulfonyl)methyl)lithium*[a]) and *Dimethyl Heptalene-4,5-dicarboxylates*



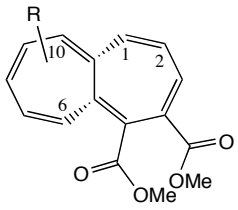
Heptalene-4,5-dicarboxylate		*Michael* Adducts[b])	
R	Nr.	Nr.	Yield [%]
H	**1**	**2**	69 – 95
1-Me	**3**	**4**	67
6-Me	**5**	**6**	67
8-Me	**7**	**8**	76
1,6-Me_2	**9**	**10**	62[c])

[a]) 1.1 Mol-equiv. of methyl phenyl sulfone were beforehand lithiated with BuLi at –10°. Larger quantities of the nucleophile lead to increasing amounts of tricyclic bis-adducts [4].

[b]) Structural assignment of the *cis*-configured adducts see later.

[c]) Methyl 1,6-dimethyl-4-((phenylsulfonyl)acetyl)heptalene-5-carboxylate was formed in minor amount (3 %).

Table 2. *Relevant Torsion Angles* Θ [°] *of Dimethyl Heptalen-4,5-dicarboxylates with Methyl Groups in* peri-*Position*[a])

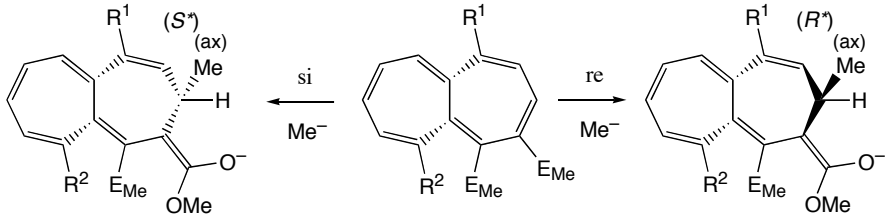


Atom Array	**3** [–73.6][b])	**5** [–71.6]	**48** [–72.6]	**45** [–107.3]
C(1)=C(2)–C(3)=C(4)	34.0	32.0 (30.3)	33.5 (33.8)	35.0 (35.4)
C(5)=C(5a)–C(10a)–C(1)	55.0	57.2 (56.1)	53.9 (56.2)	61.6 (62.6)
C(6)–C(5a)–C(10a)=C(10)	54.7	56.8 (57.8)	54.0 (59.6)	59.4 (62.0)
C(3)=C(4)–C=O	–20.8	–9.0 (–13.0)	–20.7 (–19.9)	–6.3 (–16.5)
C(5a)=C(5)–C=O	–23.6	–59.6 (–47.7)	–23.8 (–32.8)	–61.0 (–32.8)

[a]) AM1 calculated values; in parentheses X-ray data (see also *Exper. Part*, Table 7); **3** (1-Me), **5** (6-Me), **48** (10-Me), **45** (1,6-Me_2, 2-Et, 9-iPr).

[b]) In brackets AM1 calculated $\Delta H_f°$ values (Kcal·mol^{-1}).

Table 3. *Change of* Θ *(*C(5a)=C(5)–C(4)=C(OMe)O$^-$*)* [°] *on Axial* Michael *Addition of Methanide at C(3) of Dimethyl Heptalene-4,5-dicarboxylates*[a])



axial (*P**,3*S**) axial (*P**,3*R**)

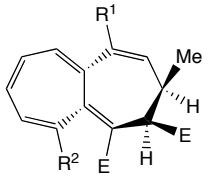
$R^1 = R^2 = H$	149.5 [–119.1]	**1**[b])	–175.2 [–123.8]
R^1 = Me, R^2 = H	144.6 [–124.5]	**3**	–175.6 [–130.3]
R^1 = H, R^2 = Me	144.9 [–124.6]	**5**	178.0 [–126.9]
$R^1 = R^2$ = Me	146.0 [–130.3]	**9**	178.2 [–133.7]

---

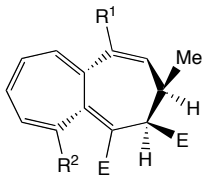
[a]) According to AM1 calculations (see also *Table 2*); in brackets ΔH_f° value of the shown axial forms.

[b]) For X-ray structure analysis of **1**, see [15].

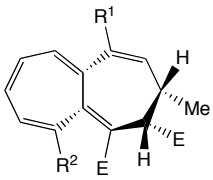
Table 4. *$\Delta H_f°$ Values* (Kcal·mol^{-1}) *of the* cis*-Diastereoisomers of Dimethyl 3-Methyl -3,4-dihydroheptalene-4,5-dicarboxylates*[a])



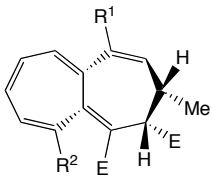
(+)-sc-(*P**,3*R**,4*R**)



(–)-sc-(*P**,3*R**,4*R**)



(+)-sc-(*P**,3*S**,4*S**)



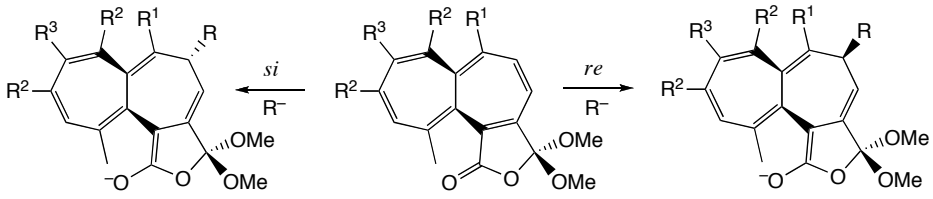
(–)-sc-(*P**,3*S**,4*S**)

R^1,R^2	Nr.[b])				
H,H	**1**	–93.75	–88.98	–92.25	–92.61
Me,H	**3**	–99.25	–95.93	–99.24	–99.45
H,Me	**5**	–98.23	–93.81	–99.09	–95.70
Me,Me	**9**	–103.91	–100.92	–105.05	–103.03

[a]) The stereochemical descriptors (+)- and (–)-sc refer to the sign of the ring torsion angle Θ (C(2)–C(3)–C(4)–C(5)).

[b]) Nr. of the corresponding dimethyl heptalene-4,5-dicarboxylate.

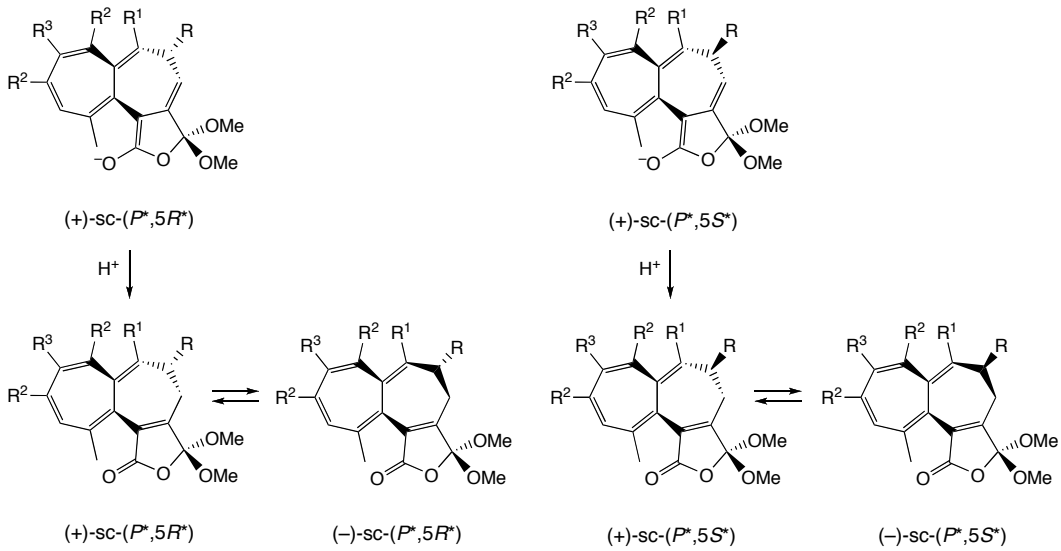
Table 5. *Dienolate Intermediates of the 1,6-Addition of Model Nucleophiles at C(5) of Heptaleno[1,2-c]furan-1-ones*[a])



Substituents	$\Delta H_f°$	Nr.	$\Delta H_f°$	$\Delta H_f°$
$R^1 = R^3$ = Me, R^2 = H; R =Me	–145.7 (42.5)	**25'**	–79.3	–146.3 (57.9)
$R^1 = R^3$ = H, R^2 = Me; R = Me	–146.6 (45.8)	**28**	–80.5	–148.5 (52.2)
$R^1 = R^2$ = Me, R^3 = H; R = Me	–151.7 (49.0)	**29**	–85.4	–152.2 (58.6)
$R^1 = R^3$ = Me, R^2 = H; R = iPr	–156.0 (47.7)	**25'**		–154.3 (62.8)
$R^1 = R^3$ = H, R^2 = Me; R = iPr	–157.1 (44.8)	**28**		–158.1 (56.3)
$R^1 = R^2$ = Me, R^3 = H; R = iPr	–161.9 (48.3)	**29**		–160.2 (63.0)

[a]) $\Delta H_f°$ in Kcal·mol^{-1}; **25'** = **25** with Me–C(8) instead of iPr–C(8); in parentheses Θ (C(3a)=C(4)–C(5)–C(6)).

Table 6. *$\Delta H_f°$ Data of Model 3,3-Dimethoxy-4,5-dihydroheptaleno[1,2-c]furan-1-ones*[a])



$R^1 = R^3$ = Me, R^2 = H; R = Me	–106.40	–102.45	–107.77	–102.29
$R^1 = R^3$ = H, R^2 = Me; R = Me	–107.19 (–116.73)	–105.35 (–114.16)	–109.74 (–119.17)	–104.76 (–113.44)
$R^1 = R^2$ = Me, R^3 = H; R =Me	–112.56 (–121.91)	–107.54 (–115.94)	–113.74 (–121.68)	–107.48 (–114.65)

[a]) Calculated with AM1; Kcal·mol^{-1}.

[b]) In parentheses values for R = iPr.

Table 7. *Crystallographic Data for Compounds* **4**, **5**, **10**, **27**, **30**, **31**, **41**, **45**, *and* **48**

	4	**5**	**10**	**27**	**30**	**31**	**41**	**45**	**48**
Crystallised from	EtOAc / hexane	ether / hexane	ether / hexane	EtOAc / hexane	EtOAc / hexane	EtOAc	^{t}BuOMe	$CHCl_3$	ether / hexane
Empirical formula	$C_{24}H_{24}O_6S$	$C_{17}H_{16}O_4$	$C_{25}H_{26}O_6S$	$C_{29}H_{34}O_6S$	$C_{27}H_{30}O_6S$	$C_{28}H_{32}O_6S$	$C_{30}H_{36}O_6S$	$C_{23}H_{28}O_4$	$C_{17}H_{16}O_4$
Formula weight [g mol^{-1}]	440.51	284.31	454.53	510.64	482.59	496.61	524.67	368.47	284.31
Crystal colour, habit	yellow-green, plate	red, prism	colourless, plate	yellow, tablet	yellow, prism	yellow, prism	yellow, plate	yellow, prism	yellow, prism
Crystal dimensions [mm]	0.11 ´ 0.35 ´ 0.37	0.30 ´ 0.42 ´ 0.50	0.10 ´ 0.26 ´ 0.48	0.07 ´ 0.22 ´ 0.25	0.08 ´ 0.15 ´ 0.22	0.10 ´ 0.12 ´ 0.27	0.05 ´ 0.20 ´ 0.22	0.17 ´ 0.20 ´ 0.32	0.23 ´ 0.25 ´ 0.47
Temperature [K]	173 (1)	173 (1)	173 (1)	160 (1)	160 (1)	160 (1)	160 (1)	160 (1)	173 (1)
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic	orthorhombic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$	*Pbca*	$P\bar{1}$	$P2_12_12_1$
Z	4	4	4	8	4	4	8	2	4
Reflections for cell determination	25	25	24	11173	29761	82443	6712	4695	25
2θ range for cell determination [°]	25 – 35	38 – 40	30 – 40	4 – 52	4 – 55	4 – 55	2 – 55	4 – 56	33 – 39
Unit cell parameters a [Å]	12.494 (2)	13.660 (2)	11.698 (2)	22.5162 (3)	16.5768(3)	14.3221(4)	14.4103 (2)	10.2548(4)	8.718 (2)
b [Å]	20.394 (2)	8.538 (2)	8.159 (4)	9.7064 (1)	8.3852(2)	11.6968(3)	17.6883 (2)	10.5119(5)	21.400 (2)
c [Å]	8.542 (2)	13.402 (2)	24.539 (2)	26.0362 (3)	18.5972(4)	14.8916(4)	20.8422 (3)	10.7388(4)	7.816 (2)
α [°]	90	90	90	90	90	90	90	61.856(2)	90
β [°]	90	114.471 (8)	101.910 (8)	109.0997 (6)	101.721(1)	92.471(2)	90	89.446(2)	90
γ [°]	90	90	90	90	90	90	90	86.063(2)	90
V [Å^3]	2176.6 (6)	1422.6 (4)	2292 (1)	5377.0 (1)	2531.10(9)	2492.4(1)	5312.5 (1)	1017.99(8)	1458.3 (5)
F(000)	928	600	960	2176	1024	1056	2240	396	600
D_x [g cm^{-3}]	1.344	1.327	1.317	1.261	1.266	1.323	1.312	1.202	1.295
μ(Mo $K\alpha$) [mm^{-1}]	0.187	0.0942	0.180	0.161	0.167	0.171	0.165	0.0808	0.0919
Scan type	$\omega/2\theta$	$\omega/2\theta$	ω	ω	ϕ and ω	ϕ and ω	ϕ and ω	ϕ and ω	$\omega/2\theta$
$2\theta_{(max)}$ [°]	55	60	55	52	55	55	55	56	60
Total reflections measured	5742	4566	5917	83621	60677	56776	76106	20553	2907
Symmetry independent reflections	5010	4142	5273	10566	5771	5720	6093	4817	2794
R_{int}	0.024	0.020	0.042	0.066	0.091	0.066	0.084	0.042	0.022
Reflections with $I > 2\sigma(I)$	3943	2979	3502	7327	4020	4332	4154	3582	1996
Reflections used in refinement	5010	4142	5480	10556	5771	5720	6087	4813	2794
Parameters refined	283	194	293	664	314	324	343	263; 13	193
$R(F)$ [$I > 2\sigma(I)$ reflections]	0.0438	0.0591	0.0480	0.0463	0.0462	0.0445	0.0451	0.0537	0.0511
$wR(F^2)$ [all data]	0.1103	0.1770	0.1297	0.1226	0.1175	0.1133	0.1222	0.1451	0.1903
Weighting parameters [a; b] [a]	0.041; 0.6247	0.0532; 1.5245	0.048; 0.858	0.0604; 0.6815	0.0523; 0.9278	0.0482; 1.3039	0.0616; 0.9896	0.0648; 0.4016	0.1127; 0.2596
Goodness of fit	1.032	1.115	1.013	1.031	1.021	1.032	1.043	1.026	1.050
Secondary extinction coefficient	-	0.016(2)	-	0.0022(3)	0.0060(8)	0.0070(9)	0.0013(3)	0.023(5)	-
Final Δ_{max}/σ	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.41; -0.19	0.42; -0.46	0.30; -0.34	0.34; -0.43	0.25; -0.35	0.27; -0.30	0.25; -0.33	0.61; -0.39	0.43; -0.31

[a] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (F_o^2 + 2F_c^2)/3$